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The Effects of Anisotropic Relaxation Times on the Hall Coefficients of some Dilute Alloys of Silver†

By J. R. A. COOPER and S. RAIMES

Department of Mathematics, Imperial College, London

[Received September 8, 1958]

ABSTRACT

A theory of the Hall effect in dilute alloys of a monovalent metal is developed, taking into account the effects of non-spherical energy surfaces and anisotropic relaxation times. The total relaxation time is assumed to be compounded of a thermal relaxation time which is anisotropic, and an impurity relaxation time which is isotropic. The wave number and the thermal relaxation time are expanded in series of cubic harmonics up to that of order four, and the conductivity and Hall coefficient are calculated in terms of the coefficients in these series. The theory is applied to some measurements made by Dorfman and Zhukova (1939) on dilute alloys of palladium, platinum, cadmium, tin, and antimony in silver, with reasonable success, but is unable to explain similar measurements made by Onnes and Beckman (1912) on the silver-gold system. The results indicate that, if a relaxation time exists, it must be considerably anisotropic, in which case it is found that the Fermi surface in pure silver need not depart from sphericity sufficiently to touch the Brillouin zone boundary.

§ 1. INTRODUCTION

A CALCULATION of the Hall and magneto-resistance coefficients of a monovalent metal, which included the effects of both non-spherical energy surfaces and an anisotropic relaxation time, was made by Davis (1939). He expressed the wave number k and relaxation time τ , in terms of energy and direction, as series of cubic harmonics, retaining only those up to order four, and his results contained parameters derived from the coefficients in these series. Davis noted that, in the absence of definite knowledge about the energy surfaces, nothing was to be gained by introducing an anisotropic relaxation time, for the effects of the latter could always be reproduced by a suitable choice of the parameters representing the shape of the Fermi surface. This was a consequence of the way in which the various parameters appeared in the formulas, and the converse was not true—it was not possible to reproduce the effects of the non-sphericity of the energy surfaces by suitable choice of the parameters representing the anisotropy of the relaxation time.

This work made it clear that measurements of the Hall and magneto-resistance coefficients of a pure metal will give only limited information about the shape of the Fermi surface, so long as the possibility of an

† Communicated by the Authors.

anisotropic relaxation time is assumed. However, measurements of the Hall coefficients of several dilute alloys of polyvalent metals in silver, carried out by Dorfman and Zhukova (1939), show results which can probably be explained only by assuming *both* non-spherical energy surfaces and anisotropic relaxation times, and make possible a partial separation of the effects of each. In the present paper an attempt will be made to account for these results by an extension of the method of Davis, and thereby to obtain some information about the Fermi surface in silver.

§ 2. THE EXPERIMENTAL RESULTS OF DORFMAN AND ZHUKOVA

Suppose a metal contains N atoms per unit volume, and there are n conduction electrons per atom. Then, if the conduction electrons are assumed to be free, it is easily shown that the Hall coefficient R is given by

$$R = -\frac{1}{Nnec}, \quad \dots \dots \dots (1)$$

where $-e$ is the charge of an electron and c is the velocity of light. It will be seen later that this formula always holds provided the energy surfaces are spherical and the relaxation time is isotropic. In general, these conditions will not apply and R will not be given exactly by eqn. (1). For the convenient presentation of the results of Hall effect experiments, however, it is useful to define a dimensionless quantity n^* by the equation

$$n^* = -\frac{1}{RNec}. \quad \dots \dots \dots (2)$$

For free electrons $n^* = n$, but otherwise n^* has no immediate physical interpretation.

Figure 1 (*a*) shows graphs of n^* against n as obtained from the results of Dorfman and Zhukova (1939) for dilute alloys of palladium, platinum, cadmium, tin, and antimony in silver. If the atomic fraction of solute is x and its valency is $1 + Z$, i.e. Z is the valency relative to that of silver, then n , the average number of conduction electrons per atom, is given by

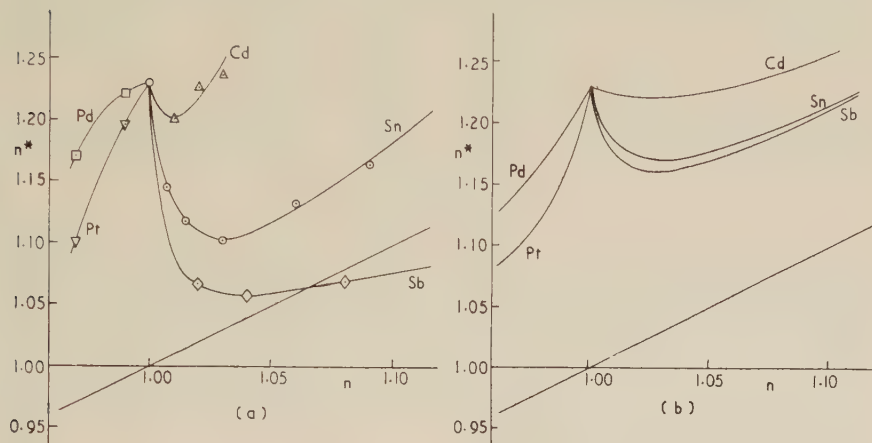
$$n = 1 + xZ. \quad \dots \dots \dots (3)$$

We take the valencies of Pd, Pt, Cd, Sn, and Sb to be 0, 0, 2, 4, and 5, so that the values of Z are -1 , -1 , 1 , 3 , and 4 respectively. The line $n^* = n$, representing the free-electron case, is also shown for comparison.

The fact that n^* is greater than unity for pure silver ($n = 1$) might be explained by the fact that the energy surfaces are not spherical. However, if this were the only explanation of the deviation from the free-electron line, we should expect all the curves to coincide in one *smooth* curve through the value for $n = 1$. It should be remembered that n^* is being plotted against n , the average number of conduction electrons per atom, in each case, and for dilute alloys we expect the Fermi surface to depend upon n only, regardless of the solute metal. The non-sphericity of the energy surfaces cannot explain the different curves obtained for

different solutes, nor can it provide an immediate explanation of the singularities in the curves at $n=1$. The only possibility of explaining the latter on these lines which suggests itself is that the Fermi surface just touches the Brillouin zone boundary in pure silver. Although this would seem a possibility in view of the recent work of Pippard (1957), it is probable that even this would not give rise to a *cusp* at $n=1$, and it certainly could not explain the appearance of different curves for different solutes. We shall discuss this question further in § 6.

Fig. 1



Curves of n^* against n , the average number of valence electrons per atom, for dilute alloys of Pd, Pt, Cd, Sn, and Sb in Ag: (a) obtained from the room-temperature measurements of Dorfman and Zhukova (1939) [N.B. only one curve is shown for each system, although Dorfman and Zhukova give sections of several others, obtained with different samples of silver]; (b) obtained from equation (22), with $A = B = -0.133$ and $C = 0.444$. The line, $n^* = n$, of the free-electron theory is shown in each case.

The most plausible explanation, which was first suggested by Coles (1956), is that the cusps are due to the different scattering mechanisms operating in the pure metal and in the alloys. In a pure metal the scattering is by thermal vibrations only, whereas in an alloy it is due to both thermal vibrations and impurity atoms. If it is assumed that the effects of the scattering can be described by a time of relaxation, then it will be seen in § 3 that, in order for this to have some bearing upon the results, the relaxation time must be anisotropic, i.e. it must vary over the Fermi surface, otherwise it does not appear in the expression for the Hall coefficient. We may in general take the total relaxation time τ to be given by

$$\frac{1}{\tau} = \frac{1}{\tau_t} + \frac{1}{\tau_i}, \quad \dots \dots \dots (4)$$

where τ_t and τ_i are the thermal and impurity relaxation times respectively. A naive picture of the processes involved would lead us to expect τ_t to

be anisotropic and, for a disordered alloy, τ_i to be isotropic. This is what we shall assume, for simplicity, in the following work, but it should be emphasized that it is by no means necessary for the success of the theory. We could, with a slight complication of the algebra, take τ_i to be anisotropic also, and it is possible that this might even improve the agreement with experiment slightly, for it would lead to a further disposable parameter in the resulting formulas.

§ 3. GENERAL THEORY

The isothermal conductivity of a metal in the presence of an electric field $\mathcal{E}$ and magnetic field $\mathcal{H}$ may be obtained by solving the Boltzmann equation

$$\frac{e}{\hbar} \left[\mathcal{E} + \frac{1}{\hbar c} \nabla_{\mathbf{k}} E \wedge \mathcal{H} \right] \cdot \nabla_{\mathbf{k}} f = \frac{f - f_0}{\tau(\mathbf{k})} \quad . \quad . \quad . \quad (5)$$

for the distribution function $f(\mathbf{k})$, and substituting the result in the formula for the current density

$$\mathbf{J} = - \frac{e}{4\pi^3 \hbar} \int f(\mathbf{k}) \nabla_{\mathbf{k}} E d\mathbf{k}. \quad . \quad . \quad . \quad (6)$$

f_0 is the value of f when $\mathcal{E} = \mathcal{H} = 0$, and $E(\mathbf{k})$ is the energy of the state $\mathbf{k}$.

The method of solution will not be given in detail because this is now standard. It was introduced by Jones and Zener (1934), and developed by Davis (1939) and also by Seitz (1950). Accounts of it have been given by Wilson (1953) and Jones (1956), and a particularly useful one from the point of view of the present work appears in an article by Blatt (1957). The general procedure is to write

$$f = f_0 - \Phi(\mathbf{k}) \frac{\partial f_0}{\partial E},$$

and neglect the product of $\mathcal{E}$ and Φ . The Boltzmann equation can then be solved for Φ by an iterative process and the result substituted in (6), which becomes

$$\mathbf{J} = \frac{e}{4\pi^3 \hbar} \int \frac{\partial f_0}{\partial E} \Phi \nabla_{\mathbf{k}} E d\mathbf{k},$$

the integral of $f_0 \nabla_{\mathbf{k}} E$ being zero by symmetry. Only terms up to order $\mathcal{H}^2$ are normally retained.

We shall confine ourselves to cubic metals and take $\mathcal{H}$ to be in the z -direction, which we shall assume to be along a cubic axis. Also, we shall take $\mathbf{J}$ in the x -direction, and $\mathcal{E}$ in the xy -plane. Thus

$$\mathcal{H} = (0, 0, \mathcal{H}_3), \quad \mathbf{J} = (J_1, 0, 0), \quad \mathcal{E} = (\mathcal{E}_1, \mathcal{E}_2, 0).$$

The isothermal Hall coefficient is then found to be

$$R = \frac{\mathcal{E}_2}{\mathcal{H}_3 J_1} = - \frac{a}{\sigma^2}, \quad . \quad . \quad . \quad (7)$$

where

$$a = \frac{e^3}{4\pi^3 c \hbar^4} \int \left(- \frac{\partial f_0}{\partial E} \right) \frac{\partial E}{\partial k_2} \tau \left(\frac{\partial E}{\partial k_2} \frac{\partial}{\partial k_1} - \frac{\partial E}{\partial k_1} \frac{\partial}{\partial k_2} \right) \left(\tau \frac{\partial E}{\partial k_1} \right) d\mathbf{k}, \quad (8)$$

and σ is the conductivity in the absence of a magnetic field, given by

$$\sigma = \frac{e^2}{4\pi^3 \hbar^2} \int \left(- \frac{\partial f_0}{\partial E} \right) \tau \left(\frac{\partial E}{\partial k_1} \right)^2 d\mathbf{k}, \quad . \quad . \quad . \quad (9)$$

Now, both the integrals are of the form

$$I = \int_0^{2\pi} d\phi \int_0^\pi d\theta \int_0^\infty \left(-\frac{\partial f_0}{\partial E} \right) G(\mathbf{k}) k^2 \sin \theta dk, \quad . \quad . \quad . \quad (10)$$

where $k_1 = k \sin \theta \cos \phi$, $k_2 = k \sin \theta \sin \phi$, and $k_3 = k \cos \theta$. In the cases we are considering it may be assumed that E is a monotonic function of k , so that the variables may be changed to E , θ , ϕ . Then

$$I = \int_0^{2\pi} d\phi \int_0^\pi d\theta \int_0^\infty \left(-\frac{\partial f_0}{\partial E} \right) G(\mathbf{k}) k^2 \sin \theta \left(\frac{\partial k}{\partial E} \right)_{\theta, \phi} dE.$$

Furthermore, if we assume complete degeneracy, so that

$$-\frac{df_0}{\partial E} = \delta(E - E_0),$$

where E_0 is the energy at the Fermi surface, the integral reduces to

$$I = \int_0^{2\pi} d\phi \int_0^\pi \left[\frac{\partial k}{\partial E} G(\mathbf{k}) k^2 \right]_{E=E_0} \sin \theta d\theta. \quad . \quad . \quad . \quad (11)$$

Thus, one integration has been eliminated. However, to offset this, the integrand in (11) is very much more complicated than that in (10). The conversion of the derivatives with respect to k_1 and k_2 to derivatives with respect to E , θ , and ϕ , changes the integrand of a , for example, from the relatively compact form shown in eqn. (8) to one which contains the sum of about one hundred terms. We shall not give this in full, but, for purposes of discussion, shall simply leave a and σ in the forms, derived from (11),

$$a = \frac{e^3}{4\pi^3 c \hbar^4} \int_0^{2\pi} d\phi \int_0^\pi \left[\frac{\partial k}{\partial E} k^2 \frac{\partial E}{\partial k_2} \tau \left\{ \tau \left(\frac{\partial E}{\partial k_2} \frac{\partial^2 E}{\partial k_1^2} - \frac{\partial E}{\partial k_1} \frac{\partial^2 E}{\partial k_1 \partial k_2} \right) + \frac{\partial E}{\partial k_1} \left(\frac{\partial E}{\partial k_2} \frac{\partial \tau}{\partial k_1} - \frac{\partial E}{\partial k_1} \frac{\partial \tau}{\partial k_2} \right) \right\} \right]_{E_0} \sin \theta d\theta, \quad . \quad . \quad . \quad (12)$$

$$\sigma = \frac{e^2}{4\pi^3 \hbar^2} \int_0^{2\pi} d\phi \int_0^\pi \left[\frac{\partial k}{\partial E} k^2 \tau \left(\frac{\partial E}{\partial k_1} \right)^2 \right]_{E_0} \sin \theta d\theta, \quad . \quad . \quad . \quad (13)$$

it being understood that, in the ultimate calculation, the derivatives must be transformed.

Two useful deductions can be made immediately:

(i) *If the relaxation time is isotropic*, i.e. if $\tau \equiv \tau(E)$, the second term in the curly brackets in (12) is identically zero. The factor $\tau^2(E_0)$ may therefore be taken outside the integral, which no longer depends upon τ_i . Similarly, $\tau(E_0)$ may be taken outside the integral in (13), and, since this occurs squared in $R = -a/\sigma^2$, the τ 's cancel and we find that R is independent of τ .

(ii) If, in addition, the energy surfaces are spherical, i.e. $E \equiv E(k)$, then all the derivatives can be evaluated directly, in terms of the derivatives of E with respect to k , and the integrations carried out. The result is as given in eqn. (1) for free electrons.

In order to explain the experimental results discussed in § 2 we shall find it necessary to assume both anisotropic relaxation times and non-spherical energy surfaces. We take τ to be as in eqn. (4), with τ_i anisotropic. We anticipate that this anisotropy will not be very great, i.e. that τ_i will not vary too drastically over the Fermi surface, and expand τ_i in a series of surface harmonics with cubic symmetry, as far as that of the fourth order. Thus we take

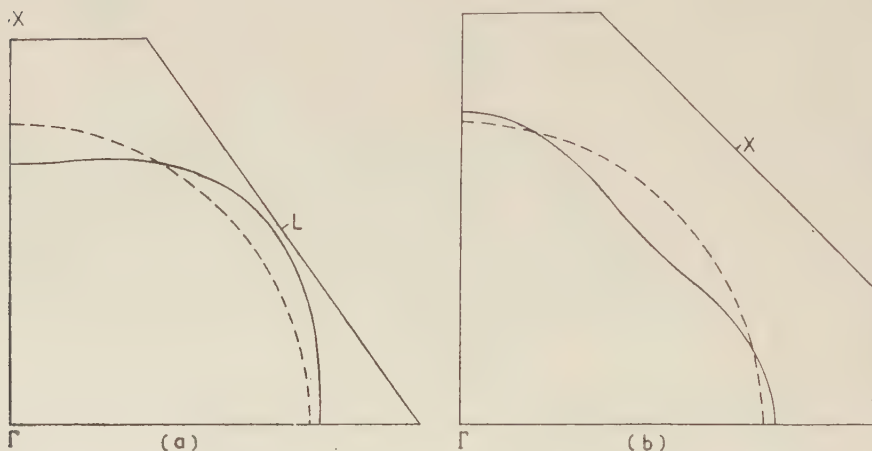
$$\tau_i = \tau_0(E) + \tau_1(E) Y_4^c(\theta, \phi), \quad \dots \quad (14)$$

where

$$Y_4^c(\theta, \phi) = P_4(\cos \theta) + \cos 4\phi P_4^4(\cos \theta)/168 \\ = x^4 + y^4 + z^4 - 3(x^2y^2 + y^2z^2 + z^2x^2), \quad \dots \quad (15)$$

and $x = \sin \theta \cos \phi$, $y = \sin \theta \sin \phi$, $z = \cos \theta$. The next such cubic harmonic is of the sixth order.

Fig. 2



Sections of the Fermi surface in pure silver, and the Brillouin zone : (a) in the plane $k_1 = k_2$; (b) in the plane $k_1 = 0$. Γ is the centre of the zone, L is the centre of a hexagonal face, and X is the centre of a square face. Section (b) has been rotated through 45° to show more clearly the shape of the surface near a square zone face—the k_3 axis passes through the point X in both cases. The broken circles are sections of the sphere which would contain one electron per atom—the distance ΓL is 1.107 times the radius of this sphere.

This was the method used by Davis (1939), who only considered a single relaxation time, however. Here we are interested in the effects of impurity content, and so include a second relaxation time, which, for small values of x , the atomic fraction of solute, we take to be

$$\tau_i = \frac{\gamma(E)}{x}. \quad \dots \quad (16)$$

To simplify the algebra, and to reduce the number of unknown functions, we let τ_i be isotropic, but, as explained in § 2, it could equally well have been taken to be anisotropic.

Similarly, assuming that the energy surfaces are not very different from spheres, we expand the wave number k in the same way as τ_l :

$$k = \alpha_0(E) + \alpha_1(E) Y_4^c(\theta, \phi). \quad . \quad . \quad . \quad (17)$$

If α_1 is positive, the energy surfaces given by this formula bulge in the directions of the axes in $\mathbf{k}$ -space, i.e. towards the square faces of the Brillouin zone. On the other hand, if α_1 is negative, the bulges are towards the hexagonal zone faces—in the (111) direction, for example. The latter is more likely, and we shall choose α_1 to be negative. Cross sections of the Fermi surface in pure silver, obtained with our ultimate choice of parameters, are shown in fig. 2.

The evaluation of the integrals (12) and (13), using eqns. (4), (14), (16), and (17), is extremely tedious and we shall merely give the final results, which are

$$\begin{aligned} \sigma = & \frac{4e^2}{3\hbar^2} \frac{\alpha_0^2 \tau_0 U}{\alpha_0'} \left[1 + \frac{4}{21} \{ 21A^2 + (2A - B)(CU - B) + C^2 U(U - 1) \} \right. \\ & + \frac{48}{1001} \{ 11A^2(CU - B) + (C^2 U^2 - C^2 U - CUB + B^2)(2A - B) \\ & \left. + C^3 U(U - 1)^2 \} \right], \quad . \quad . \quad . \quad (18) \end{aligned}$$

$$\begin{aligned} R = & - \frac{3\pi^2}{ec\alpha_0^3} \left[1 + \frac{4}{21} \{ -12A^2 + 18A(CU - B) + (CU - B)^2 \} \right. \\ & + \frac{48}{1001} \{ 135A^3 + 4(2A^2 + B^2)(CU - B) + 29A(CU - B)^2 \\ & \left. + 18ACU(B - C) + 2C^3 U^2(U - 1) - 2C^2 UB(2U - 1) + 2B^3 \} \right], \quad (19) \end{aligned}$$

where it is understood that *all functions are to be evaluated at* $E = E_0$, and

$$\begin{aligned} A = \frac{\alpha_1(E_0)}{\alpha_0(E_0)}, \quad B = \frac{\alpha_1'(E_0)}{\alpha_0'(E_0)}, \quad C = \frac{\tau_1(E_0)}{\tau_0(E_0)}, \\ U = \frac{1}{1 + \lambda x}, \quad \lambda = \frac{\tau_0(E_0)}{\gamma(E_0)}. \end{aligned}$$

These expressions are not exact, but are correct to terms of the third order in A , B , and C . It is assumed that these parameters are small compared with unity, so that, in fact, the third order terms may be neglected for our present purposes. Davis (1939) only went as far as the second order terms, and our expressions for σ and R agree with his when the third order terms are dropped and $x = 0$, i.e. for the pure metal.

It may also be shown without difficulty that the volume enclosed by the Fermi surface is

$$V = \frac{4}{3} \pi \alpha_0^3 \left(1 + \frac{4}{7} A^2 + \frac{48}{1001} A^3 \right), \quad . \quad . \quad . \quad (20)$$

and this is exact for the expansion (17). From eqn. (3), and the fact that $V = 4\pi^3 n N$, we therefore have

$$1 + xZ = \frac{\alpha_0^3}{3\pi^2 N} \left(1 + \frac{4}{7} A^2 + \frac{48}{1001} A^3 \right). \quad . \quad . \quad . \quad (21)$$

Using the value of $\kappa_0(E_0)$ given by this equation in (19), and substituting the result in eqn. (2), we obtain

$$n^* = (1 + xZ)[1 + \frac{4}{21}\{9A^2 - 18A(CU - B) - (CU - B)^2\}], \quad (22)$$

terms of higher order than the second in A , B , and C now being neglected.

Before going on to discuss the evaluation of the parameters, we wish to examine more closely a point which was made by Davis, and which has already been mentioned in § 1. If, in eqn. (22), we put $C=0$ and $x=0$, i.e. if we consider the pure metal with *non-spherical* energy surfaces, but *isotropic* relaxation time, we get

$$n^* = 1 + \frac{4}{21}(9A^2 + 18AB - B^2). \quad . \quad . \quad . \quad . \quad (23)$$

It is still possible to choose the values of A and B to give the experimental value of n^* , namely, 1.23.

However, if we set $A=B=0$ and $C \neq 0$, i.e. if we consider *spherical* energy surfaces, but *anisotropic* relaxation time, we get, for the pure metal,

$$n^* = 1 - \frac{4}{21}C^2,$$

and we cannot choose C so that $n^*=1.23$. In the extension of this to alloys, that is, with

$$n^* = (1 + xZ)(1 - \frac{4}{21}C^2U^2),$$

not only are the values wrong but the shape of the n^* curve is quite wrong, having a downward instead of an upward cusp at $n=1$.

It is clear, then, that an anisotropic relaxation time is not enough on its own to explain the experimental results. Davis concluded, however, that nothing is to be gained by taking *both* non-spherical energy surfaces *and* anisotropic relaxation times, so long as the former are taken. As pointed out in § 2, this is certainly not true for the alloy systems, because it would not result in different curves of n^* against n for different solutes, nor is it likely to produce a cusp at $n=1$.

§ 4. EVALUATION OF THE PARAMETERS

It should be noticed that A , B , C , and λ , which are the parameters we have to evaluate, are not strictly constants, but functions of E_0 , which depends upon x . In τ and k we have, in fact, five unknown functions of E . This would appear to provide considerable scope for the fitting of the theoretical to the experimental results. However, we have no reason to assume a rapid or non-monotonic variation of the parameters —unless, perhaps, the Fermi surface touches the zone boundary within the range of x which interests us, in which case the present analysis breaks down. We shall, therefore, only attempt to obtain semi-quantitative agreement between theory and experiment on the assumption that the parameters do not vary significantly with x .

In order to evaluate λ we suppose that the resistivity ρ is obtained with sufficient accuracy on taking spherical energy surfaces, i.e. $A = B = 0$. If it is further assumed that τ_0 is proportional to $E^{3/2}$, then (18) leads to

$$\lambda = \left[\left(\frac{1}{\rho} \frac{d\rho}{dx} \right)_{x=0} + 2Z \right] \left(1 - \frac{4}{21} C^2 \right), \quad . \quad . \quad . \quad . \quad (24)$$

terms of higher order than the second in C being neglected. In fact, to our degree of approximation, $2Z$ and $4C^2/21$ may also be neglected in this formula, and we may set

$$\lambda = \left(\frac{1}{\rho} \frac{d\rho}{dx} \right)_{x=0} . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

The dependence of τ_0 upon E cannot, in fact, appreciably affect this result.

Using the resistivity data of Linde (1932) and eqn. (25) we arrive at the (rounded-off) values of λ shown in the following table:

Solute	Pd	Pt	Cd	Sn	Sb
λ	25	100	20	250	450

We have found, in fact, that doubling the value of λ produces a hardly significant change in the final curves, so that the above method of evaluating λ seems quite justified.

In order to evaluate A , B , and C , we choose a constant relationship between A and B , to be discussed below, and then determine A and C to satisfy accurately the following experimental values:

- (i) the value of n^* for pure silver, and
- (ii) the value of x corresponding to the minimum of n^* in the silver-tin system, which was chosen because the minimum of the experimental curve appears to be more reliably defined for this system than for the others.

Inversion of the usual expansion of E in terms of k , θ , and ϕ , for a cubic metal, would suggest that, for small energies at least, α_0 should be proportional to $E^{1/2}$ and α_1 proportional to $E^{3/2}$. This would make $B = 3A$. We find, however, that with this relation between A and B the value of C obtained is much too great, being in the region of unity. Better values of C are obtained by taking smaller values of B/A , but it is clearly unreasonable to take this ratio less than unity, as this would imply that the bulges were becoming less pronounced as the zone boundary is approached. As a compromise we have taken A equal to B , and then find

$$A = B = -0.133, \quad C = 0.444, \quad . \quad . \quad . \quad . \quad (26)$$

which are the values used in obtaining the theoretical curves in fig. 1 (*b*). The differences between the curves are due entirely to the values of λ and of Z .

It might be thought that a better method would be to fit the two experimental values mentioned above and, in addition, the value of n^* at the minimum of the silver-tin curve, say, but we have found that these

conditions cannot be satisfied by real values of A , B , and C . A considerable amount of trial-and-error experiment has, in fact, been carried out, with different sets of empirical data, different relations between A and B , and so on, but the results have been largely negative and we shall not include them for fear of confusing the issue.

It can be seen immediately that the value of n^* given by eqn. (22) is unchanged if the signs of A , B , and C are altered simultaneously. We could thus equally well take A and B positive and C negative, but have chosen the signs so that the Fermi surface will bulge in the directions of the hexagonal zone faces, as shown in fig. 2. If third order terms were included, the value of n^* would be altered slightly on changing the signs of A , B , and C . It might be noted that, as A and C have opposite signs, the *least* value of τ occurs in the directions of the bumps on the Fermi surface.

§ 5. DISCUSSION OF RESULTS

Figure 1 shows that the theory is able to provide at least a semi-quantitative explanation of the experimental results, but several difficulties must be mentioned. In the first place, the value of the parameter C , which is $\tau_1(E_0)/\tau_0(E_0)$, is rather high. The maximum and minimum values of the function $Y_4^c(\theta, \phi)$ are 1 and $-\frac{2}{3}$ respectively, so that, with $C=0.444$, the maximum value of τ_i on the Fermi surface is about twice its minimum value—an unexpectedly large, and perhaps implausible, variation. Even with this value of C , however, the third order terms in eqns. (18) and (19) may still be neglected for our purposes, although it is not certain that one is justified in neglecting the sixth order harmonic in the expansion of τ_i .

It does not seem possible, within the bounds of the present theory, greatly to improve the depths of the theoretical minima without assuming unreasonable values of the parameters. As explained in § 4, A and C were fixed so as to give the minimum of the theoretical silver-tin curve at the correct value of n , or of x . Unfortunately, this results in a considerable displacement of the minimum of the silver-cadmium curve. The positions of all the minima may be fixed roughly as in the experimental curves by suitable choice of the parameters, for example,

$$A = -0.123, \quad B = -0.214, \quad C = 0.500, \quad . \quad . \quad . \quad . \quad (27)$$

but the minima are then found to be much shallower even than those of the curves in fig. 1(b), which are themselves by no means deep enough. Which set of values is to be preferred is largely a matter of choice—the values of A and C , in which we are most interested, are not significantly different in the two cases.

It should be remarked that lack of complete agreement between theory and experiment in the present case need not cause undue pessimism, for the accuracy of the experimental results is not known. It seems that Hall effect data are not only regrettably small in number but generally rather unreliable. The experiments of Dorfman and Zhukova have not been repeated, as far as we know, and so one is hesitant to accept them

without question. Certainly, different samples of silver gave rise to large changes in the curves, particularly for the silver-cadmium system. It might be added that only the values of R for the silver-tin system were tabulated—the others had to be measured from diagrams. It seems possible, for example, that the different curvatures of the experimental and theoretical curves for the silver palladium and silver-platinum systems may as well be due to slight experimental errors as to flaws in the theory.

A more serious difficulty is discovered in the case of the silver-gold system. This system was not investigated by Dorfman and Zhukova, but some experimental results of Onnes and Beckman (1912) show the value of n^* rising as x increases. Since silver and gold are both monovalent, the value of n remains constant at unity, and the results cannot be plotted in fig. 1 [but see, for example, fig. 1 of the paper by Coles (1956), mentioned earlier, in which n^* is plotted against x for this system]. However, it is easily deduced from eqn. (22) that, according to the present theory, n^* must decrease monotonically as x increases, at least for the range of x in which we are interested. The reason for this is simply that the square-bracketed factor in (22) decreases monotonically with increasing x in all cases, and the minima and eventual rise of the curves are due entirely to the factor $1+xZ$. Now in the silver-gold system this factor is unity, so that n^* cannot reach a minimum in the dilute alloy range we are considering. It is found, in fact, that λ has the value 20 for this system, as it has for the silver-cadmium system. Consequently, the curve of n^* against x for silver-gold will at first decrease slightly more rapidly than the silver-cadmium curve, but it will not rise again.

It must be confessed that there seems no way of explaining this discrepancy on the basis of our present theory. If, as is possible, the values of A , B , and C are chosen to give a rise of n^* against x for the silver-gold system, then the minima of all the systems investigated by Dorfman and Zhukova are lost. Admittedly, the work of Onnes and Beckman is rather old, but it seems hardly likely that experimental deficiencies would give rise to a curve of n^* against x with slope of the wrong sign. However, we must leave this question in abeyance until these experiments have been repeated with smaller values of x than those considered by Onnes and Beckman.

We have said nothing so far about the temperature dependence of n^* . The measurements of Dorfman and Zhukova were, in fact, all made at room temperature. If our assumptions regarding τ_l and τ_i are correct, then, as the temperature is lowered to absolute zero, n^* should decrease and all the curves in fig. 1 should tend to coincide in a smooth curve—approximately a line parallel to the free-electron line. Experimental data are here completely lacking. Admittedly, Onnes and Beckman carried out their measurements at 290°K and at 20°K, but the temperature dependence which they obtain is again inexplicable, for they find that, on lowering the temperature, n^* decreases for the pure metal but increases for the alloys.

§ 6. THE FERMI SURFACE

Figure 2(a) shows the closest approach to the Brillouin zone boundary of the Fermi surface for pure silver, according to the present theory and the values of the parameters given in (26). The surface does not touch the boundary, nor would it do so in the alloy systems until beyond the minima of the curves in fig. 1. Unfortunately, as we have had to be content with only partial agreement with experiment, there is a certain arbitrariness in this result. If, however, we had assumed an isotropic relaxation time, it is easily determined from eqn. (23) that, depending upon the relation between A and B , the Fermi surface would probably touch, or very nearly touch, the zone boundary in pure silver—with $A = B$ it would certainly touch. This possibility was overlooked by Davis.

Recently, Olsen and Rodriguez (1957) have made magneto-resistance measurements on copper, silver, and gold at temperatures of 4°K and 20°K , and have attempted to analyse them by a method similar to that of Davis. They assume, with some justification, that an isotropic relaxation time exists in this temperature range, and indeed our own assumptions regarding τ_l and τ_i would also lead to this conclusion. However, even though they include the sixth order cubic harmonic in their expansion of k , Olsen and Rodriguez were unable to choose their parameters in such a way as to fit their experimental results exactly. They found that the values of the parameters which gave the best fit in the case of copper were such as to cause the Fermi surface to touch the Brillouin zone in the (111) direction, and they concluded that this is probably what happens, in agreement with the deduction of Pippard (1957) for copper. No definite conclusions were reached regarding silver and gold.

Although it is quite clear that the nature of the Fermi surface alone would not suffice to explain *all* the results of Dorfman and Zhukova, it is interesting to consider whether the touching of the zone boundary could, in fact, cause a cusp in the n^* curve. If this were so, it might, together with the anisotropy of the relaxation time, offer a means of reconciling the experimental results for the silver-gold system with the others, for in the silver-gold system the Fermi surface does not swell with increasing x . As an elementary approach to this problem, we have considered the case of spherical energy surfaces in a simple cubic zone, and have allowed the Fermi surface to expand until it touches the zone boundary, thereafter taking the integrals (12) and (13), with isotropic τ , only over that part of the surface inside the zone. We find that the curve of n^* against n does not have the required cusp, but it does have a discontinuity of slope at the point of touching the zone boundary. The curve is at first the line $n^* = n$, as shown in fig. 1, and it becomes almost horizontal and slowly decreasing—a further rise in the curve, on this model, could only be caused by overlap into the second zone. It seems very likely, however, that even this discontinuity of slope is due to the artificiality of the model. The true Fermi surface, after it touches, must meet the zone faces orthogonally, and so its curvature near the zone boundary must gradually

change from that in our model to one with opposite sign. Putting this another way, the Fermi surface must always be smooth in extended $\mathbf{k}$ -space, and this is not so for the present model. It is probable, therefore, that the touching of the zone boundary in a real alloy system would simply cause a smooth bend in the curve of n^* against n , and would be of little help in explaining the results of Dorfman and Zhukova.

More with the intention of formally rounding off the present theory than in the hope of reaching any radically new conclusions, we are now extending our calculation to allow τ_i to be anisotropic as well as τ_v , and taking all the expansions as far as the sixth order cubic harmonic. This is extremely tedious, and, even if agreement with experiment is enhanced, it will probably be at the expense of increased arbitrariness in the evaluation of parameters, of which there will be twice as many. It is our opinion that there will be no real progress in this field until a larger number of reliable measurements have been made, on very dilute alloys and over a wide range of temperatures.

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The Resistance of Diamond to Abrasion†

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ABSTRACT

The resistance of diamond to abrasion by the conventional method of diamond polishers, using a cast-iron scaife with diamond powder, is extremely sensitive to the orientation of the stone. Thus the rate of removal of material is known to vary by a factor of over a hundred along different directions on a cube face. This anisotropy has been investigated by measurements of the rate of wear on facets in the zone [010]. Other experiments have been undertaken to elucidate the mechanism responsible for the wear. It is concluded that abrasion proceeds as the result of mechanical processes rather than by thermal ones, as has sometimes been suggested. Measurements with a diamond impregnated wheel show that the basic hardness variations on a diamond are comparatively small. The large anisotropy observed with the conventional method is not a fundamental property of the diamond, but is associated with the use of loose powder.

§ 1. INTRODUCTION

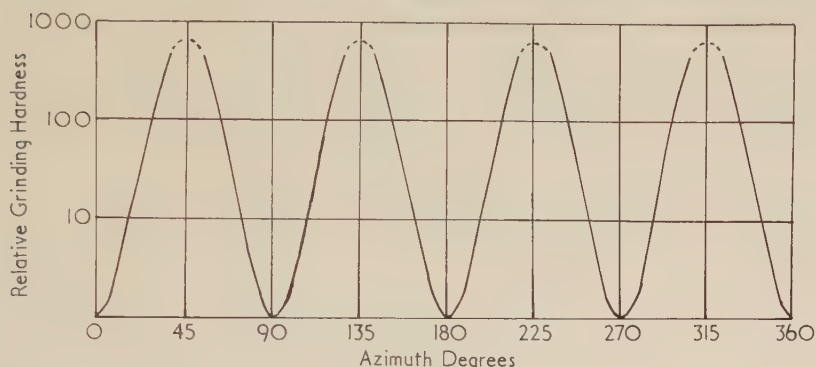
THE resistance of diamond facets to abrasion by the normal grinding and polishing techniques varies remarkably both with the crystallographic orientation of the facet and with the direction of abrasion. A cube face is comparatively easy to grind in directions parallel to the crystallographic axes, but over 100 times harder in directions at 45° away from them (Tolkowsky 1920, Denning 1953, Hukao 1955, Scott 1957) as is shown in fig. 1. An octahedron face is always extremely hard, while some directions on a dodecahedron face are softer than any on a cube (Denning 1957). Although there have been several attempts to account for this wide variation of the hardness, all the treatments appear incomplete. Indeed there is still no agreement as to whether abrasion proceeds by mechanical fracture (e.g. Tolkowsky 1920) or by thermally activated chemical changes (e.g. Seal 1957). In this paper we describe some measurements of the hardness variation, and discuss what light they throw on the nature of the abrasion process.

In the usual grinding and polishing techniques the diamond is pressed against the face of a cast-iron wheel or 'scaife', charged with diamond powder, and rotating at high speed about a vertical axis. Previous authors have measured hardness variations by grinding down surface layers parallel to the surface being tested, but the method is slow and wasteful of material, and it is difficult to ensure that the new facets are parallel to the original surface. The present measurements have been

† Communicated by the Authors.

made with the Grodzinski micro-abrasion tester (Grodzinski *et al.* 1949) which abrades the diamond in a rather similar way to a cast-iron scaife, but permits rapid and sensitive measurements to be made on carefully oriented facets (Wilks and Wilks 1954). A small cut is made on the diamond with the edge of a rotating cast-iron double conical wheel, charged with diamond powder in olive oil; unless otherwise stated the $\frac{1}{2}$ in. diameter wheel was run at about 5000 r.p.m. under a load of 200 g for periods of 20 sec. The depth of the cut is determined by multiple beam interference techniques, and its inverse is taken as a measure of the hardness.

Fig. 1



Relative grinding hardness plotted against azimuth for a cube plane (after Denning 1953).

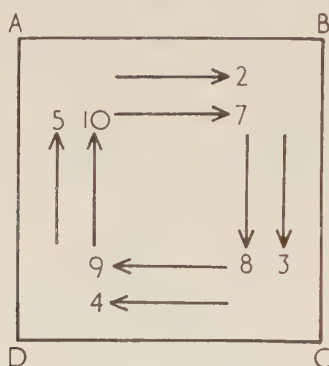
It is well known (see Grodzinski 1953) that the hardness of diamond is very much a function of how it is measured. For example, Peters *et al.* (1945) demonstrated that the grinding rates may be considerably increased by striking an electric arc between the stone and the scaife. Also variations in hardness are greatly reduced if the measurements are made with diamond impregnated or sintered wheels. The values of the hardness obtained with the Grodzinski tester exhibit the great sensitivity to orientation which is characteristic of the normal grinding process, and the method is therefore well suited for the present investigations. Finally, we mention that all our measurements have been made on good quality gem stones so as to eliminate spurious effects due to inhomogeneity in the diamond.

§ 2. THE VARIATION OF ABRASION HARDNESS IN THE ZONE [010]

We have previously discussed the importance of making measurements on correctly oriented facets (Wilks and Wilks 1954). The results of this section confirm our previous results and give interesting new light on an earlier suggestion of irregular behaviour. Measurements were made on specially cut planes, which lay in the zone [010] to within 30 min of arc. The layout of cuts on a typical facet is shown in fig. 2, together with the

order and direction in which they were made. In directions AB and CD the cuts are parallel to a cubic axis. The first and sixth cut of each series were made on a cube facet of a separate stone which served as a reference plane; these cuts were parallel to each other and in the same direction. Thus the hardness of each direction on a facet could be obtained in terms of the hardness of the reference stone, and our results are not affected by variations in the characteristics of the abrading wheel. (The cast-iron wheels tend to blunt after about ten cuts, and therefore for each facet we used a new wheel of the same dimensions made from the same block of iron.) The depths of each pair of parallel cuts in the same direction agreed to within about 10% and this figure sets the limit of our accuracy.

Fig. 2



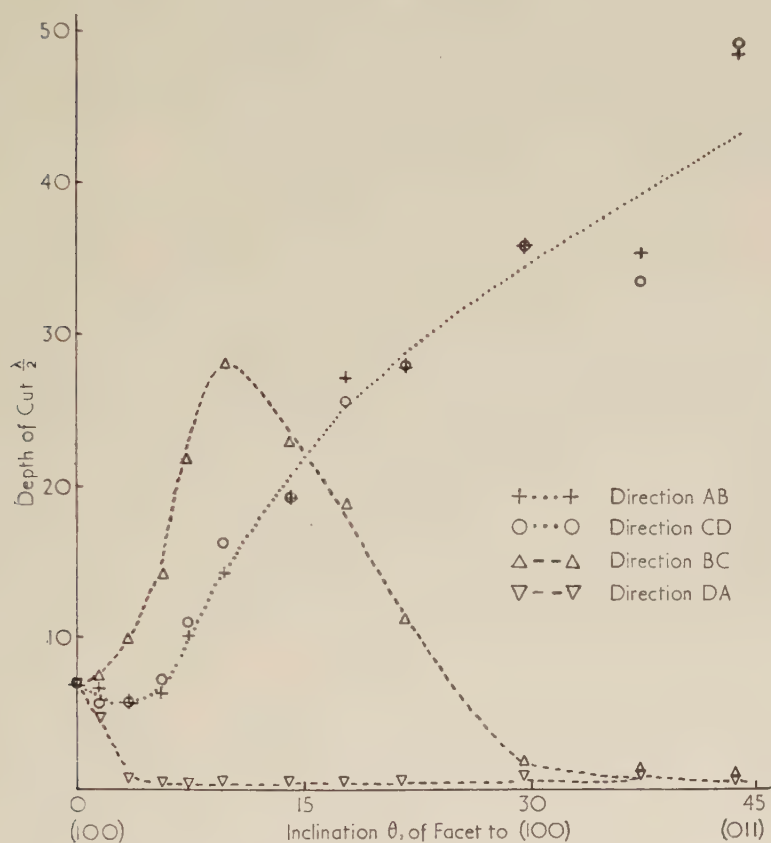
The layout of cuts on a facet in the zone $[010]$. The facet was polished down from AB so that in successive facets CD was below AB.

Figure 3 shows the average depth of cut in each direction plotted against θ the inclination of the facet to (100) . Of course, these depths are not immediately comparable with figures given by other workers for the rate of removal of material when flat surfaces are ground down on a scaife. The depth of a cut depends on the area of contact, and on the angles at which the wheel is attacking the stone; both these parameters change as the wheel deepens its cut, and it was found experimentally that the depth is roughly proportional to the square root of the time of abrasion. The depth of cut therefore increases more rapidly for small cuts and our results will *underestimate* the hardness variations. However, this is of no great consequence in any of the arguments we shall use.

When the facet coincides with (100) all the cuts are parallel to crystal axes and there is no difference between their depths to within the experimental error. In the directions AB and CD, which remain parallel to crystal axes, the depths increase steadily with increasing θ , as has previously been observed by Tolkowsky (1920). (The small initial decrease is within the experimental error.) The results for the directions BC and DA confirm our earlier experiment; although the direction DA gets

steadily harder, the direction BC is softer than any of the others for $\theta < 15^\circ$. This effect is not described by Tolkowsky, probably because he was unable to obtain facets accurately positioned in the [010] zone and he therefore smoothed his results to what he thought would have occurred had the facets been in the zone. Denning (1955) has reported grinding tests on a facet 5° from (100) in the zone [010] which shows a rather similar behaviour, although as his measurements were at the limit of resolution he does not discuss the point in detail.

Fig. 3



The variation of hardness on facets in the zone [010].

Kraus and Slawson (1939) have made the empirical generalization that on a given facet the easiest directions of abrasion are those parallel to the longest projection of the crystallographic axis. Every facet in the zone [010] contains one axis, therefore abrasion should take place most easily in the two directions parallel to it. Also, as the dodecahedron plane is easier to abrade in these directions than the cube, the hardness in these two directions should decrease steadily as the facets are displaced from

the cube towards the dodecahedron plane. Similarly, the hardness in the two directions perpendicular to this axis should steadily increase. The experimental results show that the situation is considerably more complex, but reconcile the four-fold symmetry of the diamond with the experience of diamond polishers (Grodzinski 1953) that one of the four principal directions on a cube face is often appreciably easier to abrade than the others. It has previously been shown that four-fold symmetry is only exhibited by facets oriented to within at least 30 min of true cube planes (Wilks and Wilks 1954), and we have subsequently confirmed this result on cube planes set up on a further ten stones in the course of other work. The present experiments show that for a misalignment of 5° the values of the hardness in the four principal perpendicular directions are in the ratio 1 : 2 : 2 : 30. Therefore any discrepancy between theory and practice is almost certainly due to diamond polishers having worked on facets lying several degrees away from true cube planes.

§ 3. THE EFFECT OF SPEED AND LOAD ON THE RATE OF ABRASION

Tolkowsky has shown that the rate of removal of material when grinding with powder on a cast-iron scaife is proportional to the speed of the scaife, and we have made similar experiments with the micro-abrasion tester running at different speeds. In order to obtain an accurate comparison of very different rates of wear, the times of abrasion were selected so as to produce approximately the same depth of cut in each case. Our results on two stones are shown in table 1; these correspond to linear velocities of about 4 to 360 cm/sec, while Tolkowsky used speeds of 1500 to 9000 cm/sec. Over a wide range of velocities about the same depth of cut is obtained for the same total number of revolutions, thus the rate of abrasion appears to be proportional to the speed of the wheel.

Table 1

	Stone A					Stone B	
Wheel speed (r.p.m.)	5400	2750	1100	580	5400	60	530
Time of abrasion (sec)	20	39	98	186	20	1660	200
No. of revolutions	1800	1790	1800	1800	1800	1660	1780
Depth of cut ($\lambda/2$)	4.4	3.6	3.5	3.5	3.2	4.6	4.0

It is well known that the surfaces of even well polished materials are very irregular if viewed under sufficient magnification, and present a system of valleys and jagged hills or asperities; for well polished diamonds the heights of these asperities may be of the order of 100 Å (Wilks, E. M.,

1953). On rubbing two surfaces together, intense local heating is produced in the region of the asperities, and the polishing of a metal comes about by surface melting at these hot spots (Bowden and Tabor 1950). It has previously been suggested that the wear of diamond during grinding is due either to burning at the hot spots (see for example Grodzinski 1953), or more probably by graphitization at a somewhat lower temperature (Seal 1957). There have also been frequent observations that either graphite or amorphous carbon is formed on the diamond during abrasion (see for example Scott 1957), and flashes of light are sometimes visible in the surface of a stone being abraded.

Previous thermal treatments have failed to account for the great anisotropy of the hardness, but Seal and Scott point out that the excess temperature of the hot spots is proportional to the coefficient of friction measured in the appropriate direction. As the rate of any thermal transformation depends exponentially on the temperature, comparatively small differences in the coefficient of friction may make a great difference to the hardness, and Seal has shown that the coefficient of friction for a diamond stylus sliding over a cube plane, at speeds of the order of 1 mm/sec, varies by a factor of almost 2 for different azimuthal angles. Of course, one still has to explain why the coefficient of friction should vary by this factor, but this is a more tractable problem.

One cannot make an exact estimate of the temperature of the hot spots, but according to Bowden and Tabor the excess temperature of the asperities on two surfaces sliding over each other is proportional to v the relative linear velocity of the two surfaces, at comparatively low speeds, and to $\sqrt{v}$ at higher speeds. Thus the range of wheel speeds used in the present experiments was sufficient to change the excess temperature of the asperities by a factor of at least $\sqrt{10}$. If abrasion is a thermally activated process then such a change should have an enormous effect on the rate of wear. This is not observed and the present results appear inconsistent with a thermal mechanism. (It is perhaps possible that the temperature of the hot spots reaches a limiting value which is independent of the speed of the wheel, but in this case it is difficult to explain the anisotropy.) The results show that each revolution of the wheel removes the same amount of material whatever its speed, and this follows naturally in mechanical theories of the abrasion process. The presence of any amorphous carbon or graphite on the surface of abraded diamonds is almost certainly a consequence of the high temperatures generated during the abrasion process, but the transformation must be a secondary effect which does not much affect the rate of wear.

A review of other papers concerning abrasion as a thermal mechanism has been given by Grodzinski, but the experimental evidence is rather sparse and not always consistent. For example, Dawihl and Fritsch (1941) suggest that the abrasion process is one of burning, and give results which apparently show that abrasion only occurs in the presence of oxygen, but Scott has shown that the wear of diamonds polishing glass is independent

of the surrounding atmosphere. Of course, diamond can be attacked by a burning process at sufficiently high temperatures as is described for example by Wollheim (1903) and by Dawihl and Fritsch (1936), but this is a quite different technique from that of grinding with a cast-iron scife.

We have also confirmed Tolkowsky's result that the rate of grinding is proportional to the load on the stone. Table 2 shows that the number of revolutions required to produce a certain depth of cut varies approximately as the inverse of the load on the wheel.

Table 2

Speed (r.p.m.)	530	530	60	60
Load (g)	200	10	200	50
Time (min)	3.3	67	28	111
No. of revs	1750	35500	1680	6660
Depth ($\lambda/2$)	3.95	5.40	4.60	5.05

As the stress between the powder and the stone is limited to the yield stress of the cast iron, the effect of increasing the load is only to increase the area of contact in direct proportion to the load. This type of dependence of the grinding rate on load would probably be obtained whether abrasion were a thermal or mechanical process.

§ 4. THE VARIATION OF ABRASION HARDNESS ON CUBE FACETS

The variation of the hardness on cube facets has been described by several authors including Tolkowsky (1920) and Denning (1953) whose results are shown in fig. 1. All these authors report variations of the order of 100 to 1, and similar results have been obtained with the micro-abrasion tester. Thus abrading a cube face for 20 sec in one of the soft directions parallel to the axes made a cut of depth $5(\lambda/2)$, but an attempt to make a similar cut in a direction at 45° to the axes produced hardly any effect. The depth of the cut was less than $\lambda/50$, and the cast-iron wheel was appreciably blunted.

No crystal other than diamond has been reported to show such large variation of the hardness. The classical example of an anisotropic crystal is kyanite on which the scratch hardness varies by a factor of about 2, but there is little information on the hardness of crystals as measured by abrasion tests. We have therefore made tests on polished cube faces of germanium and silicon, both of which have the same structure as diamond, although of course there is an electronic contribution to the binding energy. The tests were similar to those on diamond, save that a variety of wheels (cast iron, brass, copper, lead and aluminium) were used. In most

cases the wheels were run without abrasive powder, but in a few tests on germanium, powdered germanium and diamond were also employed. As both germanium and silicon have relatively low thermal conductivities and low melting points, particular care was taken to avoid surface melting and the abrading wheel was rotated slowly by hand. Tests were made every $22\frac{1}{2}^{\circ}$ through 360° on cube faces of both crystals; no significant variation in the abrasion hardness was detected. In particular no variation was observed when germanium was abraded with germanium powder in order to simulate the abrading conditions used on diamond. Thus it appears that the diamond type lattice is not in itself responsible for the large directional effects shown by diamond, nor is the effect primarily the result of abrading a substance with its own powder.

Scratch tests were made by abrading the cube face of one diamond with an ordinary diamond glass cutting tool, set so that the working edge was the intersection of two octahedron faces. The tests were only qualitative, but showed that scratches could be made with about the same ease in the hard and soft directions. Subsequent cuts with the micro-abrasion tester confirmed that this face was quite typical and exhibited the usual high ratio of hardness in the two directions. On replacing the cast-iron wheel charged with powder by an impregnated (sintered) wheel of the same size, the ratio of the depths in the two directions was reduced from several hundred to about $1\frac{1}{2}$. On extending the experiments with another type of impregnated wheel, the ratio of the depths was reduced to values between 4 and 7. Similar cuts could also be made on the dodecahedron and on the extremely hard octahedron face; these were of about the same size as those made in the soft direction of a cube face with a cast-iron wheel. Thus there appears to be no fundamental property of diamond which is some hundreds of times stronger in one direction than another: only a difference which is greatly magnified by the method of abrasion.

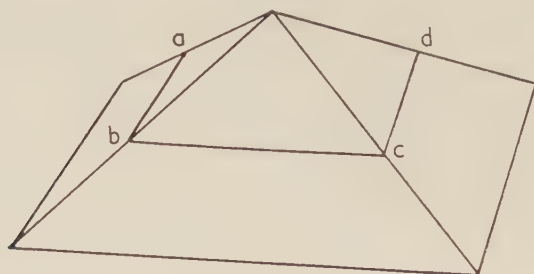
§ 5. THE BASIC HARDNESS DIFFERENCES

Tolkowsky (1920) regarded abrasion as a purely mechanical process in which the asperities on each surface break off as they collide. He treated the variation of the resistance to abrasion by considering a model made up of elementary blocks consisting of either regular octahedra or tetrahedra. He deduced that an octahedral face is very hard because the elementary blocks always present a smooth surface, whereas on cube and dodecahedron facets they present a rough jagged surface which permits of abrasion. A detailed consideration of the way in which these blocks buttress each other together leads to the correct qualitative variation of hardness in the different directions on cube and dodecahedron planes. A rather similar treatment has also been proposed by Berghheimer (1938).

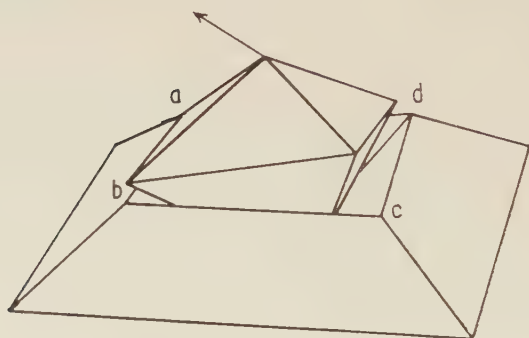
Of course, a diamond is not built up of such similarly sized units, and its surface will but barely approximate to that of the model. Although not a great deal is known of the details of the surfaces, studies of etched

faces confirm that their structure has the same general form, or symmetry, as that of the model (Schultink *et al.* 1954, Tolansky 1954). The intersections of the cleavage planes at the surface of the stone will trace out a system of hills and valleys of the same form as those of the model, and it is possible to reach the same conclusions by more satisfactory arguments.

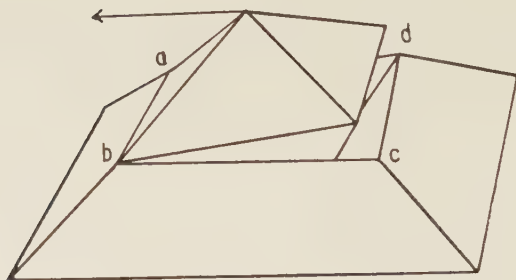
Fig. 4



(a)



(b)



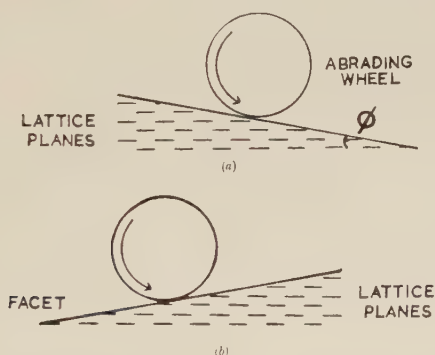
(c)

Diagram to illustrate cleavage at the tip of an octahedron.

On Tolkowsky's model a cube face presents a jagged surface consisting of the upper halves of regular octahedra standing above the general level

of the surface; on a real diamond the surface asperities, although irregular, will still be bounded by the cleavage planes. We believe that the differences in hardness arise essentially from the different resistance to cleavage of these asperities when attacked in different directions. The essence of the matter may be seen by considering the force required to cleave off the top of the regular octahedron shown in fig. 4(a). In this diagram $abcd$ define a cube plane, and we assume for simplicity that the cleavage fragment will be a regular octahedron. If a stress is applied along the line ca , parallel to a cube axis, it is possible for cleavage to commence at the corner c and spread out simultaneously along the faces cb and cd , as in fig. 4(b). However, if the stress is applied at an angle of 45° to the axis, say along cb , it will tend to rotate the cleavage fragment about ab (fig. 4(c)), cleavage would have to take place simultaneously along the faces cb , cd and da , and this is highly unlikely. In a real diamond the irregular shapes of the asperities will permit cleavage to take place more readily in this direction, but probably less so than in directions parallel to the axes. Octahedra faces are very hard because the cleavage fragments will be laminae parallel to the faces, and these present only a small area to the abrading stress. The variations on a dodecahedron face may be accounted for by rather similar considerations as apply to the cube face; moreover, in the soft direction the asperities will present a particularly large area to the abrading stress, so that this direction is the softest on any face.

Fig. 5



Diagrams to show possible orientations of facets close to the cube plane (not to scale). (a) Direction of abrasion BC. (b) Direction of abrasion DA, (After Wilks, E. M., and Wilks, J., 1954.)

The above mechanical picture also accounts for the anomalous behaviour of the hardness in the zone $[010]$ mentioned previously, namely that in the direction BC the hardness does not steadily increase from the cube to the dodecahedron orientation but first decreases somewhat. Figure 5, which is taken from Wilks and Wilks (1954), shows the orientation of the

facet with respect to the lattice planes for the directions of abrasion BC and DA. When the facet is tilted as in fig. 5(a), the surface asperities will present a greater area to the abrading force and be less securely buttressed in position than is the case when the tilt is as in fig. 5(b). Thus as the facet moves away from the cube orientation there is an initial tendency for this direction to become softer.

§ 6. THE HARDNESS DIFFERENCES WITH SCAIFE AND POWDER

Although Tolkowsky claimed to explain the variations in hardness observed in grinding experiments, his treatment only accounts for the more basic differences, and does not show why the variations are much greater when measured with a cast iron than with a sintered wheel. This behaviour can, however, be associated with the use of loose powder in the normal grinding process and we now consider the mechanism of abrasion in more detail.

During abrasion, each particle of diamond powder projecting from the surface of a sintered wheel will be brought against the asperities of the stone, and as the wheel rotates it will be pushed forward until it (a) cleaves off the asperity, (b) rides over it, or (c) is itself cleaved off. The wear of the wheel resulting from this last process is much greater when a hard direction of a stone is being attacked, and the wheel becomes appreciably blunted after a few cuts. However, in the softer directions the rate of grinding will be determined by the relative probabilities of the particles on the wheel cleaving off or riding over the asperities on the stone.

If the sintered wheel is replaced by a cast-iron wheel charged with loose powder, powder may be removed from the wheel when it strikes an asperity, and this possibility may greatly magnify the variations in hardness. Suppose that the mean force necessary to cleave off a given asperity in a certain direction is f_A , and that the mean force required to remove a particle from the cast iron is f_B . Then if $f_A > f_B$ most of the particles will be removed from the wheel, whereas if $f_A < f_B$ material is removed from the stone. There is very little information about the interactions between the powder and cast-iron scaifes, it is only known that certain unspecified porous types of cast iron make good scaifes, presumably because the powder is able to obtain a good seating within the pores. Thus even with the most suitable choice of cast iron it seems likely that the two critical forces f_A and f_B will be of similar magnitude, so that it is quite plausible for f_B to be greater than f_A in a soft direction and less than f_A in a hard direction. In this case one would observe a normal rate of grinding in the soft direction, but in the hard directions the powder would be removed from the wheel and hardly any abrasion be produced on the stone. In practice there will be a considerable range of grain size and dimensions of the pores so that f_A and f_B will have a range of values and the effect will be somewhat blurred over. Nevertheless, any basic hardness differences in the diamond will be greatly exaggerated.

The above treatment implies that the nature of the oil used in charging the wheel with diamond dust should affect the hardness variation, in particular a more 'sticky' oil should help retain the particles and reduce the variations. Table 3 shows the depths of cuts made on a cube face with wheels charged with powder and olive oil and castor oil respectively. In each case two cuts were made parallel to a soft direction, then two cuts in a somewhat harder direction 10° away, and finally two more cuts in the original soft direction; the use of the castor oil results in a deeper cut in the harder direction.

Table 3

Depth of Cut		
Direction	Olive Oil	Castor Oil
0°	5.7	4.4
0°	4.3	4.2
10°	1.4	2.2
10°	1.1	2.1
0°	1.8	3.9
0°	1.6	4.2

It is to be noted that the wheel charged with castor oil made the same depth of cut in the soft direction after abrading in the harder direction. Thus the reduction in the depth of the cuts 10° away from the soft direction cannot be accounted for entirely by a removal of particles from the wheel. If this were so the reduced depths would imply that at least one particle in two was removed from the wheel, and one would therefore expect the depths of subsequent cuts in the soft directions to be reduced. (As is the case if olive oil is used.) Thus it appears that when a particle of powder strikes an asperity on the stone, it may be displaced in its seating in a pore of the cast iron and therefore does not abrade, but is nevertheless retained on the wheel by the surface tension or stickiness of the oil.

§ 7. CONCLUSION

The present experiments were designed to investigate the great anisotropy in wear resistance shown by diamonds when abraded on a conventional cast-iron scaife with diamond powder. It appears that this abrasion proceeds by mechanical processes rather than thermal ones, although it is certainly possible to wear away diamond by burning as has been done by Dawihl and Fritsch. The large directional effects arise because the powder is loose and is more readily removed from the scaife in some directions than others, and this greatly exaggerates the basic

hardness differences of the diamond. These differences are quite small and are comparable with those observed in other crystals.

The results on the variation of the hardness in the zone [010] serve to emphasize the importance of working on correctly oriented facets. Thus the experience of diamond polishers that one direction on a cube face is often much easier to abrade than any other is almost certainly due to the facet being incorrectly aligned with respect to the crystal lattice.

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Some Properties of Crystals of Silver Chloride containing Traces of Copper Chlorides†

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ABSTRACT

A number of properties of crystals of silver chloride containing traces of copper chlorides have been investigated with the microscope. It has been found that the dislocations remaining after annealing in crystals which contained originally 0.1 mol % of cupric chloride are decorated by the separation of a second phase during cooling. Crystals containing cuprous chloride have a high photosensitivity but the products of photochemical change fade on storage. Valuable observations have been made on arrays of dislocations in well annealed and recrystallized specimens and on dislocations introduced by plastic deformation. With these crystals it has been possible to demonstrate that the space required for the separation of further silver atoms upon a silver particle inside the crystal is made available by the formation of prismatic dislocation loops which glide away from the interface between the particle and the surrounding crystal. This is a new phenomenon in the physics of the solid state which has not been previously described.

§ 1. INTRODUCTION

THE photosensitivity of mixed crystals of silver and cuprous bromides was studied by Clark and Mitchell (1956) during the course of their experimental work on the formation of the photographic latent image. As far as the formation of the latent image was concerned, they found that the properties of such crystals were not very different from those of pure silver bromide. The mixed crystals had, however, a remarkably high sensitivity for the formation of a visible image during exposure. This has also been noted by Moser *et al.* (1957) for crystals of silver chloride containing copper chloride and there seems little doubt that at least some of the single crystals of silver halides which were used in earlier work (Hilsch and Pohl 1930, Löhle 1933) on changes in optical absorption during exposure were sensitized with cuprous ions.

The main purpose of the investigation which will be described in the present paper was to study with the microscope the nature and distribution of the products which are formed during the exposure of crystals of silver chloride which contained initially cupric or cuprous chloride. Interesting new observations have been made.

† Communicated by the Authors.

§ 2. EXPERIMENTAL METHODS

Globules of pure silver chloride were prepared as described by Clark and Mitchell (1956). Anhydrous cupric chloride was prepared by dehydrating $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ of 'Analar' quality at room temperature in continuously evacuated all-glass apparatus. The water vapour was condensed in a trap cooled with liquid air. The temperature was finally raised to 50°C and pumping continued for a further hour. Anhydrous cuprous chloride was prepared from cupric chloride by the method recommended by Gröger (1901).

For the mixed crystals, silver chloride and anhydrous cupric chloride were melted together in an atmosphere of chlorine using the apparatus shown in figs. 1 and 2 of the paper by Clark and Mitchell (1956). The molten material was filtered and then converted into globules of suitable size for the preparation of thin sheet crystals. Globules for the preparation of mixed crystals of silver and cuprous chlorides were prepared in the same way but hydrogen chloride or nitrogen was, in this case, used as a protective gas. Thin sheets were prepared from silver chloride containing between 0.001 and 1 mol % of cupric chloride and from silver chloride containing between 0.0014 and 1.4 mol % of cuprous chloride. The results which will be presented in this paper have, however, all been obtained with crystals containing 0.01 or 0.1 mol % of cupric chloride or else 0.07 mol % of cuprous chloride.

After their separation from the glass plates (see Clark and Mitchell 1956), the thin sheets were cut into pieces and annealed in sealed-off tubes at a temperature of 420°C for periods up to 18 hours. Crystals prepared from silver chloride to which cupric chloride had been added were annealed for 18 hours in chlorine at a pressure of 300 mm Hg at 420°C while the crystals to which cuprous chloride had been added were also annealed for 18 hours in oxygen-free nitrogen at a pressure of 200 mm Hg at 420°C . The main purpose of annealing in sealed tubes in a gas atmosphere is to reduce evaporation and thermal etching both of which spoil the surfaces of the specimens.

§ 3. EXPERIMENTAL OBSERVATIONS

3.1. *Crystals of Silver Chloride containing Cupric Chloride*3.1.1. *Internal decoration of dislocations*

These crystals are a yellowish-brown colour when they are removed from the furnace after having been annealed in chlorine. The colour fades gradually and crystals which contained originally 0.001 mol % of cupric chloride have finally the same visual appearance of those of pure silver chloride. Crystals which contained 0.01 or 0.1 mol % remain a very pale yellowish-brown. The corresponding absorption spectrum has been measured by Moser *et al.* (1957).

The microscopic examination of crystals which contained 0.1 mol % of cupric chloride under intense dark field illumination shows that they

are not optically clear. The dislocations which remain at the end of the annealing period (18 hours at 420°C) are decorated throughout the thickness of the crystals with discrete particles which are efficient scatterers of light. Tilt and twist sub-boundaries, three-dimensional internal arrays of dislocations, dislocation loops and helical dislocations of many kinds and dimensions are all made visible within the crystals (figs. 1, 2 and 3†). There is a low density of randomly distributed scattering particles, particularly in the recrystallized areas around the edges of the specimens and, consequently, good contrast between the dislocations and the dark background. This provides a powerful method for studying the arrays of dislocations which remain after specimens have been annealed at a temperature of 420°C for periods between 8 and 18 hours. As might have been anticipated, the same phenomena are observed when crystals containing more than 0.14 mol % of cuprous chloride which have been heated in chlorine for similar periods are examined with the microscope under intense dark-field illumination. No segregation occurs when crystals with lower concentrations of cupric and cuprous chloride are annealed in chlorine.

Well-defined etch pits are produced where the dislocations meet the surface when the crystals are dipped in a 3N solution of sodium thiosulphate for a fraction of a second (see Jones and Mitchell 1957).

3.1.2. *Decoration of dislocations with photolytic silver*

Crystals containing cupric chloride are insensitive to light when they are removed from the furnace after having been annealed in chlorine and no change in the appearance of the internal decoration of the dislocations, which was described in the previous section, is produced by exposure. As the yellowish-brown colour fades with storage, the photolytic sensitivity of the crystals rises. Silver then separates along dislocation lines during exposure to a depth of about 30 microns below the surface. The dislocations in the surface regions are densely and continuously decorated with silver. There is a low density of randomly distributed particles of silver in the recrystallized areas around the edges of the specimens so that the dislocations of the residual tilt and twist sub-boundaries are decorated with good clarity and contrast.

In crystals containing 0.1 mol % of cupric chloride there is complete continuity between the arrays of dislocations in the surface regions as made visible for bright field examination by the separation of photolytic silver and the arrays in the interior which are decorated as described in the previous section. The dislocations are particularly clearly decorated with photolytic silver during the exposure of crystals to which 0.01 mol % of cupric chloride has been added but there is usually no internal decoration by scattering particles at this concentration (fig. 4).

† All figures are shown as plates.

Dislocations introduced into the surface regions by plastic deformation are also made visible by the separation of photolytic silver. Glass spheres with a mean diameter of 3 microns have been incorporated in silver chloride crystals containing 0.01 mol % of cupric chloride. All the phenomena reported by Jones and Mitchell (1958) in crystals of pure silver chloride have been observed.

3.2. *Crystals of Silver Chloride containing Cuprous Chloride*

3.2.1. *Examination before exposure to light*

All the crystals of silver chloride containing cuprous chloride which were prepared were found to be optically clear when they were examined with intense orange yellow dark-field illumination after having been annealed for 8–18 hours in nitrogen at a pressure of 200 mm Hg at 420°C.

3.2.2. *The photosensitivity of the crystals*

The sensitivity of crystals of silver bromide containing cuprous bromide was noted by Clark and Mitchell (1956). Two photochemical changes occur when the crystals are exposed for a few seconds at a distance of 25 cm from a 125 watt medium high-pressure mercury-vapour lamp. Particles of photolytic silver separate within the crystals and a deep blue-green coloration appears which fades steadily with storage after exposure.

When crystals of silver chloride containing 0.07 mol % cuprous chloride are similarly exposed, the same two photochemical changes are observed. A blue-violet coloration is produced, which fades rapidly during the first few minutes after the end of the exposure, and discrete particles of photolytic silver separate. The crystals have been examined with intense white and orange-yellow illumination from a well-corrected dark-field condenser at successive stages during exposure and during the fading of the blue-violet coloration and the photolytic silver.

Particles which scatter light and are assumed to be of photolytic silver are formed in the dislocations within a few seconds of the beginning of the exposure and this photochemical change is accompanied by the appearance of the uniformly distributed blue-violet coloration. Apart from scattering due to the silver particles in the dislocations, the crystals are optically clear at this stage; the coloration is not due to the presence of discrete scattering particles and randomly distributed particles do not appear when it fades. After an exposure of more than twenty seconds under the above conditions, sub-microscopic particles appear which are distributed throughout the elements of the sub-structure. The blue-violet coloration again fades rapidly after the completion of the exposure without any accompanying change in the appearance of either the decorated dislocations or the sub-microscopic particles. It seems that the coloration of the crystals and the separation

of particles of photolytic silver during exposure represent two independent phenomena. The colloidal particles which separate along the dislocation lines and within the sub-structure elements suffer regression to a certain extent when the exposed crystals are stored for a few months so that it is necessary to make permanent photomicrographic records of configurations of dislocations soon after exposure. The fading of both the coloration and the particles is accelerated by warming the specimens and also by exposing them to red light. The coloration does not appear when specimens are exposed at higher temperatures.

3.2.3. *The decoration of the dislocations with photolytic silver*

Crystals of silver chloride which contain 0.07 mol % of cuprous chloride have a greater sensitivity than pure crystals for the separation of particles of photolytic silver along dislocation lines during exposure. Because of this it has been possible to make many new observations with them on the behaviour of dislocations during plastic deformation. Provided that the strains are less than 0.1% individual dislocations on glide planes are clearly resolved (fig. 5). Glass spheres have been incorporated in the crystals (see Jones and Mitchell 1958) and the systems of prismatic dislocations which are generated during cooling have been studied (fig. 6). The decoration of the dislocations during the exposure of crystals containing cuprous chloride never extends beyond 30 microns from the surface but, within this region, all the characteristic annealing structures, including tilt and twist sub-boundaries and three-dimensional arrays of dislocations have also been observed.

In crystals containing cuprous chloride which have been annealed in nitrogen, a considerable background of randomly distributed colloidal particles always appears during exposure. The presence of this background reduces the contrast compared, for example, with crystals of pure silver chloride. The visibility of the dislocations is also impaired, if the exposure is prolonged, by the phenomenon which will be described in the next section.

3.2.4. *The separation of particles of silver*

A new phenomenon is observed in crystals containing 0.07 mol % of cuprous chloride which have been annealed in nitrogen and given exposures of several minutes. When the crystals are examined with the microscope, larger particles, assumed to be of silver, are seen. These are usually distributed along dislocation lines, and are located at the centres of roughly spherical volumes within which there is a low density of the randomly distributed sub-microscopic particles. The larger particles are surrounded by systems of decorated prismatic dislocation loops, figures of eight, and concentric helical dislocations (figs. 7-11) in precisely the same way as are the glass spheres in the experiments of Jones and Mitchell (1958). The systems of prismatic dislocations extend along the twelve

$\langle 110 \rangle$ directions which radiate from the central particle. They are similar to those surrounding precipitated gold particles in silver chloride crystals which are illustrated in fig. 2 of the paper by Bartlett and Mitchell (1958). The individual prismatic dislocations are, however, more clearly resolved in the present case.

Our observations leave little doubt that both the central particles and the systems of prismatic dislocations are formed during the exposure of the crystal. We have already mentioned that the crystals are optically clear before exposure and that no discrete scattering centres can be observed within the elements of the sub-structure during the earliest stages of exposure. A random distribution of very small particles then appears and those within roughly spherical volumes aggregate to form the larger central particles. The systems of prismatic dislocations surrounding the particles are produced at this stage and subsequently decorated by the silver which is liberated and redistributed during further exposure.

§ 4. INTERPRETATION OF THE OBSERVATIONS

4.1. *Experiments with Crystals of Silver Chloride containing Cupric Chloride*

4.1.1. *The separation of a second phase along the dislocations*

Our experimental observations show that cupric chloride has a limited solubility in silver chloride at low temperatures which increases as the temperature increases. The cupric chloride passes into solid solution when crystals of silver chloride containing about 0.1 mol % of either cupric or cuprous chloride are annealed in chlorine at 420°C for 8–18 hours. The solubility falls on cooling and the supersaturation in cupric chloride consequently rises. Nuclei of a second phase rich in cupric chloride are then formed in the dislocations and increase to visible size during further cooling.

The mechanism responsible for the fading of the yellow-brown coloration shown by the crystals after they have been annealed in chlorine has not been established. When the crystals are annealed at 420°C *in vacuo*, chlorine is liberated and the copper ions pass from the cupric to the cuprous state. We therefore suggest that the partial fading of the yellow-brown coloration during storage is due to the lowering of the free energy by the formation of some cuprous chloride, which has a higher solubility in the crystals than cupric chloride, and the escape of chlorine from the surface. This implies that a cupric ion on a lattice site introduces an acceptor level to which an electron can be raised from the full band by thermal activation at room temperature. The positive holes which are created in this way diffuse to the surface, together with the vacant cation lattice sites which compensated the excess positive charges of the cupric ions, and chlorine escapes. For this reason, in specifying the composition, we have referred to crystals which, for example, “contained originally 0.1 mol % of cupric chloride”.

4.1.2. Behaviour of the crystals during exposure

The characteristic features of crystals of silver chloride which initially contained 0.01 mol % of cupric chloride are (1) the low-density background of randomly distributed particles of silver which appears within the crystals and upon their surfaces during exposure and (2) the high density of the silver particles which separate along the dislocation lines. The presence of the divalent cupric ions during annealing reduces the equilibrium concentrations of the mobile positively charged lattice defects. Consequently fewer randomly distributed internal cavities will be produced in these crystals by the condensation of pairs of Schottky defects which may be present in significant concentrations in crystals of pure silver chloride at temperatures near the melting point. Nuclei of silver are also effectively destroyed when the crystals are annealed in chlorine. The operation of these two factors reduces the number of sites which are active within the elements of the sub-structures for the condensation of silver atoms during the early stages of an exposure and therefore increases the amount of silver which separates on nuclei formed along the dislocation lines. Small nuclei, consisting of groups of silver atoms, are also probably preferentially destroyed in crystals containing cupric ions: the larger nuclei, which grow to visible size, may carry a positive charge, due to adsorption of silver ions and therefore not trap positive holes; the smaller nuclei, which are uncharged (Mitchell 1957), capture positive holes and suffer regression.

4.2. Experiments with Crystals of Silver Chloride containing Cuprous Chloride

4.2.1. Decoration of dislocations and fading of photolytic silver

These crystals have (1) a high sensitivity for the appearance of a blue-violet coloration during exposure and (2) a characteristic instability of the photochemical products. The nature of the centres responsible for the coloration has not been established. The fading of the photolytic silver shows that an amount of chlorine, equivalent to the photolytic silver which separates, does not escape from the crystal during exposure. The positive holes may be trapped in these crystals by the cuprous ions to form cupric ions (see also Moser *et al.* 1957) which are themselves, like cadmium ions in silver chloride crystals, unable to trap conduction electrons. The electrons would then combine with interstitial silver ions to form silver atoms along the dislocation lines leaving an equivalent number of cupric ions and vacant silver ion lattice sites in the crystal. If the thermally activated transference of electrons from the valence band to acceptor levels associated with the cupric ions were to create positive holes, these, together with vacant silver ion lattice sites, could diffuse to the silver particles and cause the observed fading and regression. The occurrence of the same electronic transition following the absorption of a light quantum would account for the rapid fading of the colloidal

particles which has been observed when the crystals have been irradiated with red light.

The separation of the silver particles is not mainly confined to the dislocation lines as in crystals of pure silver chloride or in those containing initially 0.01 mol % of cupric chloride. The randomly distributed colloidal particles which can be seen in all the photomicrographs probably separate in internal cavities formed by the condensation of Schottky defects during cooling. The cavities must, however, be too small to scatter light because the crystals are found to be optically clear when they are examined with intense dark field illumination.

These crystals have some advantages over pure crystals for the study of the behaviour of the dislocations during plastic deformation on account of their greatly increased photolytic sensitivity but the visibility of the dislocations is reduced by the background.

4.2.2. *Prismatic dislocations and the separation of particles of silver*

The mechanism by which space is made available for the separation of particles of photolytic silver within crystals of silver halides has never been properly understood (see Mitchell and Mott 1957). The recognition of the fact that dislocations provide sites upon which internal silver can separate (Hedges and Mitchell 1953) did not resolve the difficulties because particles of silver of visible size could not form along dislocation lines without the participation of some mechanism whereby both silver and halide ions were removed from the interface between the silver particle and the silver halide. No such mechanism can be readily envisaged which would operate at room temperature in a crystal in which the lattice disorder is of the Frenkel type. Seitz (1951) with clear insight remarked that "the colloidal particle may be surrounded by a large volume which is relatively densely covered with dislocations which have been pushed out from the colloidal spot" and that "if prismatic slip could occur, it might permit spherical precipitates to grow to any size since the stress would be relieved by such slip". The observations reported in § 3.2.4 indicate that the growing particle of silver does indeed strain the lattice beyond the elastic limit and that the strain is relaxed through the generation of systems of prismatic dislocation loops by the mechanism described by Jones and Mitchell (1958). The mutual repulsion of these loops causes them to glide away from the interface so that successive discs of silver halide are removed to make room for the separation of further silver atoms. This provides a sound and effective mechanism for the relaxation of a compressive stress field in a crystal which deforms by pencil glide. Its operation during the formation of precipitate particles has been illustrated in a particularly clear way in the experiments with crystals of silver chloride containing 0.07 mol % of cuprous chloride. It is further discussed in a paper by Harvey and Mitchell on the precipitation of gold in sodium chloride crystals.

Both the prismatic dislocations and the internal cavities are probably made visible in these crystals because the positive holes are trapped by cuprous ions and thus prevented from causing the regression of small silver nuclei. Fresh nuclei for the separation of silver can therefore be formed around newly created dislocation loops during the later stages of an exposure ; this would not occur in crystals of pure silver chloride or in crystals containing cupric chloride.

ACKNOWLEDGMENTS

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On the Knight Shift of Alloys†

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ABSTRACT

The change and broadening of the Knight shift of silver produced by various solute elements are explained by the fluctuations in electronic density produced at long range by each solute atom. The change in Knight shift observed for Cd, In, Sn and Sb solutes are in satisfactory agreement with those computed using a free electrons approximation for the matrix. From the sign and the values of the changes observed for Pd and Pt solutes, it is concluded that most of the screening arises there from an emptying of their d shells, especially for Pt. Finally the change and broadening of the Knight shift of the solute elements are explained in the same way.

RECENT measurements by Drain (1958) and Rowland (1958) have shown that the Knight shift of silver is markedly reduced by addition of various solute elements (Cd, In, Sn, Sb, Pd, Pt). The decrease is nearly proportional to the solute concentration in the whole range of solubility. Also the lines broaden with concentration. Finally, in **Ag** Cd alloys, the shift of cadmium is reduced with increasing concentration of cadmium, and at nearly the same rate as the shift of silver.

These observations are in contradiction with earlier and probably less accurate measurements on other alloys (Knight 1956) and Friedel's argument that the Knight shift of the matrix should not be affected by the very short range perturbations produced by the solute elements (Friedel 1955). The changes in Knight shift are about ten times too large to be possibly due to a size effect: their proportionality to concentration makes them unlikely to be due to interactions between impurities or to zone boundary effects.

It has been, however, re-emphasized recently by Brooks‡ that, besides the short range perturbations (mostly within the atom itself) which provide the necessary screening, there occur around an impurity atom changes of electronic density which oscillate with the distance and reach a fairly long range. These are for instance responsible for the magnetic coupling of the nuclei via the conductive electrons (Ruderman and Kittel 1954, Bloembergen and Rowland 1955). We want to point out that these

† Communicated by the Authors.

‡ A general formula for this effect was given by Friedel (1952); cf. Friedel (1958) for a more complete study.

long-range fluctuations of electronic density explain very satisfactorily the variations of Knight shift observed in silver alloys. We think that they explain their broadening, too.

Let η_l be the phase shift produced on the l th spherical harmonic by the highly localized perturbing potential of a solute atom when acting on the Fermi electrons, treated here as free electrons. Outside the solute atom, where the perturbing potential is negligible, a spherical harmonic $Y_l^m j_l(kr)$ has then been replaced by $Y_l^m [j_l(kr) \cos \eta_l - n_l(kr) \sin \eta_l]$. j_l and n_l are respectively the spherical Bessel and Neumann functions of order l , k the wave number at the Fermi level and r the distance from the solute atom. Taking account of the density of states at the Fermi level, one deduces easily that the presence of the solute atom creates a relative change of electronic density per unit energy at the Fermi level and per unit volume at distance r :

$$\frac{\Delta\rho(r)}{\rho} = \sum_l (2l+1) \{ [n_l^2(kr) - j_l^2(kr)] \sin^2 \eta_l - j_l(kr) n_l(kr) \sin^2 \eta_l \}. \quad (1)$$

As long as the solute atoms scatter independently, this fluctuation in electronic density can be averaged over all the lattice sites R_i surrounding a silver atom and over all silver atoms. This gives the relative change in the Knight shift $K = \Delta r/r$ of silver atoms proportional to the solute atomic concentration c :

$$\frac{\Delta K}{K} = C_M c$$

with

$$C_M = \sum_i \frac{\Delta_i(R_i)}{\rho}. \quad (2)$$

The following table shows that the observed values of the constant C_M , from Drain (1958) and Rowland (1958), agree satisfactorily with the values obtained using eqns. (1) and (2).

Values of the Change in Knight Shift $C_M = \Delta K/Kc$

Solute	Observed		Computed
	Drain (1958)	Rowland (1958)	Eqns. (1) and (2)
Cd	-0.35	-0.4	-0.1
In		-0.7	-0.7
Sn		-1.1	-1.1
Sb		-1.2	-1.0
Pd	-0.3	-0.6	-1.6 (+0.4)
Pt			-1.6 (+0.4)

For Cd, In, Sn, Sb, the phase shifts used are Blatt's, which take into account both valency and size effects (Blatt 1957). For Pd and Pt, the

same method, which assumes a screening by the repulsion of conduction electrons leads of course to an effect of the same size as for Cd, but positive (+0.9). We obtain on the contrary an effect somewhat too large, but of the right negative sign (-1.3), by assuming that the screening is obtained by partially emptying a virtual d level which takes the place of the d shell of the transitional element (Friedel 1956); this is equivalent to assuming that all the screening is in the d component. The experimental values suggest an intermediary situation, where screening is obtained simultaneously by both mechanisms, with a fuller, thus more stable, d state for Pd than Pt. This is in agreement with other experimental evidences (cf. Hoares and Yates 1957 for the electronic specific heat of Ag Pd, Friedel 1956 for other evidences).

The line broadening produced can be deduced from eqn. (1) by a method of second moment. This has not been worked out yet, but it is clear from eqn. (1) that at small concentrations there will be a large number of practically unperturbed silver atom. The width of the line must therefore be at least of the same order as its shift, as is observed.

Finally, these fluctuations must shift and broaden the Knight shift of the solute atoms in a very similar way. Let R_A^B be the ratio of the electronic densities (per unit volume and unit energy) at the bottom of the conduction band and on the nuclei, for two pure metals made respectively of B and A atoms; and let $X_A^B R_A^B$ be the ratio of the electronic densities (per unit volume and unit energy) at the Fermi level of an alloy AB on a B nucleus and on an A nucleus away from any B atom. If K_B is the Knight shift of B at infinite dilution in A, it is easily shown that one should have

$$\frac{\Delta K_B}{K_B C_B} = \frac{\Delta K_A}{K_A C_B} / X_A^B. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The ratio X_A^B is of course positive; and, it is near to unity, according to Knight's experimental rule (Knight 1956). The relative changes in Knight shifts of both solvent and solute atoms should thus vary in a similar way with solute concentration. This is indeed observed in Ag Cd, where the value of X_{Ag}^{Cd} deduced from experiment and eqn. (3) is 1.15. An identical value has been recently computed by one of us, in a theoretical study of Knight's rule (Daniel 1958).

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Measurements of the Optical Constants of Mercury and Mercury-Indium Amalgams in the Spectral Region 4000 to 17 000 cm^{-1} †

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ABSTRACT

The optical constants of liquid mercury have been measured by a reflection method, in the infra-red spectral region 4000 to 17 000 cm^{-1} . The apparatus used has two quartz Rochon prisms, a quartz prism spectrometer, and a lead sulphide photocell. The reflecting surface was a free surface of mercury, which could be enclosed in a hydrogen filled tank. The measured values do not agree with the predictions of the Drude free electron theory. The dielectric constant ϵ has a minimum at a wave number $\sim 9 \times 10^3 \text{ cm}^{-1}$. The temperature variation of the optical constants of mercury has been investigated between 20° and 230°C. Measurements have been made of the optical constants of mercury-indium amalgams, between 0 and 33 atm % indium.

§ 1. INTRODUCTION

THE experimental values of Kent (1919) for the optical constants of liquid bismuth, lead, cadmium and tin, indicated that all the valence electrons in these metals behave as free electrons when excited by visible or ultra-violet radiation. This can be explained if the energy of visible quanta ($\sim 2.5 \text{ eV}$) is much greater than the binding energy of the valence electrons. Further, the conductivity, σ , calculated from the optical constants, when extrapolated to zero frequency using the Drude theory for free electrons, is nearly equal to the static conductivity, σ_0 . This indicates that all the valence electrons are contributing to the static conductivity and therefore that their binding energy is zero. On the other hand, the theory of the change in σ_0 on melting (see Mott and Jones 1936) assumes only a small change in the number of conduction electrons on melting for lead, cadmium and tin, and the number of conduction electrons in the solid metals is less than one per atom. It is hoped that the present measurements in the infra-red spectrum will show whether the valence electrons in liquid metals are free or bound with energies below 2.5 eV.

§ 2. PREVIOUS WORK

Meier (1910) measured the optical constants of mercury confined in a cell attached to one face of a glass prism. Two possible systematic errors arise with this method. The first is due to a thin film of air adhering to the prism face even when the cell is filled with mercury. The second is

† Communicated by the Author.

due to strain double refraction in the glass prism. A strain producing a differential phase shift of a few degrees can cause serious errors. These two sources of error have been considered by Schulz (1957) who used a similar arrangement of cell and prism to produce a reflecting surface of mercury.

Several workers have used a free surface of mercury for reflection measurements. Wheeler (1911) made a careful study of a surface cleaning method for mercury. His measurements on a mercury surface in contact with air and various transparent liquids showed that the mercury surfaces he obtained could be considered as free of any contamination having an appreciable effect on the optical properties. The same method of surface cleaning was used by O'Brien (1926) in extending the measurements to other points in the visible and ultra-violet spectrum. Beattie and Conn (1955) give values for the optical constants of mercury at a single point in the infra-red spectrum ($1.66 \times 10^3 \text{ cm}^{-1}$).

§ 3. METHOD OF MEASUREMENT

A reflection method using two polarizers was chosen for the measurement of optical constants. The second polarizer is set at 45° to the plane of incidence and the first polarizer is rotated. It is assumed that the radiation arriving at the first polarizer is unpolarized. This has been checked experimentally (see below). The intensity transmitted by the second polarizer is a sinusoidal function of the position angle, ϕ_1 , of the first polarizer. The amplitude ratio and phase of this intensity variation are measured. They lead to values of the auxiliary angles η and γ , whence the refractive index, n , and the extinction coefficient k , can be calculated (see Hodgson 1955). For comparison with theory and electrical measurements, it has been found more convenient to calculate the dielectric constant, ϵ ($\epsilon = n^2 - k^2$) and the conductivity in e.s.u., σ ($\sigma/c = nk$); k is the wave number in cm^{-1} .

§ 4. APPARATUS

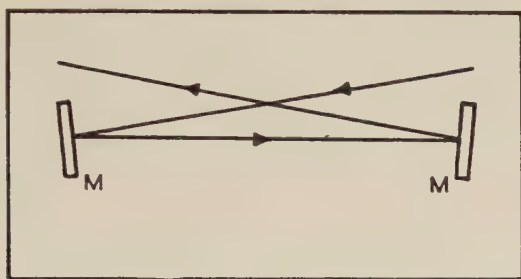
The source of radiation is a tungsten ribbon lamp. Radiation emitted nearly normally from the face of the ribbon is collected by a concave mirror and forms an image of the ribbon on a circular hole of 1 mm diameter. From the symmetry of this arrangement, the radiation passing through the hole should be unpolarized. After two more reflections the radiation passes through a Rochon prism. The effect of these reflections on the polarization has been estimated using a simple formula (Hodgson 1956). The degree of polarization caused by reflections before the first polarizer is < 0.001 . The undeviated beam from the Rochon prism forms a six-fold magnified image of the hole on a circular aperture just in front of the reflecting surface.

The mean angle of incidence, θ , is 81.5° . The spread in θ is determined by a rectangular aperture placed over the concave mirror receiving the reflected radiation. The spread is $\pm 0.15^\circ$ about the central ray. After

reflection the radiation passes through a second Rochon prism and the undeviated beam is focused on the entrance slit of a spectrometer. The spectrometer has two concave mirrors and a fused silica prism in a Littrow arrangement. The radiation from the exit slit falls on a lead sulphide cell.

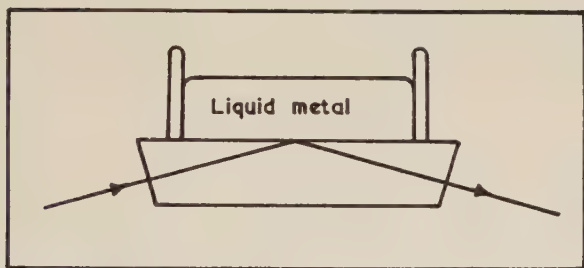
The radiation is chopped at about 900 c/s and a photoelectric cell provides a reference signal for a phase sensitive rectifier. The signal from the lead sulphide cell is passed to a tuned amplifier followed by a rectifier and d.c. amplifier. A phase sensitive rectifier is used to obtain good linearity. To test the linearity and the zero polarization of the source, the reflecting surface was replaced by a pair of plane mirrors as shown in fig. 1. The polarization introduced by the two reflections is

Fig. 1



Two mirrors. M=plane mirror, front aluminized.

Fig. 2



Fused silica cell and prism.

negligible. When the first polarizer was rotated, the measured intensity variation was within 0.5% of the theoretical function, $\cos^2(\phi_1 - \alpha)$, where α is a constant. The resolving power of the spectrometer has a minimum value of about 10 near $k = 10^4 \text{ cm}^{-1}$. The usable spectral range with the ribbon lamp is from 0.4 to $1.7 \times 10^4 \text{ cm}^{-1}$. With a mercury vapour lamp measurements can be made up to $2.7 \times 10^4 \text{ cm}^{-1}$, but the accuracy is low because of fluctuations in the intensity of radiation from the lamp.

It was the original intention to make a reflecting surface of liquid metal by enclosing it in a silica cell on a silica prism, as shown in fig. 2. Measurements on a fused silica prism showed appreciable double refraction,

leading to errors in the measurement of phase change on reflection. The apparatus was therefore rearranged to use the reflection from a free surface of liquid metal.

§ 5. EXPERIMENTAL RESULTS FOR MERCURY

Mercury was purified by distillation under a pressure of a few centimetres of air. The method described by Wheeler (*loc. cit.*) was used to make a clean surface on mercury. A simultaneous overflow at several points on the edge of the container was achieved by careful levelling. The surface was cleaned by overflow before measurements at each point in the spectrum. Measurements at one point took about 5 min. The values of $(-\epsilon)$ and (σ/c) given in table 1 are the means of two measurements at each point. The probable errors for one measurement have been estimated at three spectral points and are indicated by the vertical lines in fig. 3. These probable errors were calculated from estimated probable errors in the angles γ , η and θ ; for example, at $\log k = 3.92$ the estimated probable errors are $\pm 0.1^\circ$, $\pm 0.1^\circ$ and $\pm 0.05^\circ$, respectively. The results of Wheeler, who used sodium light and $\theta = 60^\circ$, agree with the present results.

Table 1. Mercury. Measured Values for a Surface Cleaned by the Overflow Method. Means of Two Measurements

$\log k$	3.62	3.670	3.752	3.822	3.922	4.030	4.136	4.216	$\times 10^4$
$-\epsilon$	21.2	24.9	30.1	33.4	35.3	33.8	28.7	23.4	
σ/c	34.6	34.2	33.4	32.7	30.8	25.7	20.0	14.9	

k = wave number in cm^{-1} .

ϵ = dielectric constant.

σ = conductivity in e.s.u.

The overflow method of cleaning would be difficult to apply to metals other than mercury. It was therefore desirable to get an idea of the rate of contamination of a clean mercury surface standing in air or vacuum. It was found that the measured values of ϵ and σ for mercury in air did not change appreciably up to 30 min after cleaning. Thereafter a gradual change occurred, but the changes in 60 min were only of the order of the probable errors. The changes with mercury in a vacuum or hydrogen atmosphere were similar. Measurements on mercury filtered through a fine glass tube into a silica boat gave values of ϵ and σ close to the values for a clean surface. Approximate values of ϵ and σ were measured at three points in the visible and ultra-violet, using a mercury lamp as source of radiation. The agreement with O'Brien's values obtained with a similar surface is satisfactory (fig. 4). There are large discrepancies with Schulz's values obtained with a mercury-glass surface.

§ 6. DISCUSSION OF RESULTS

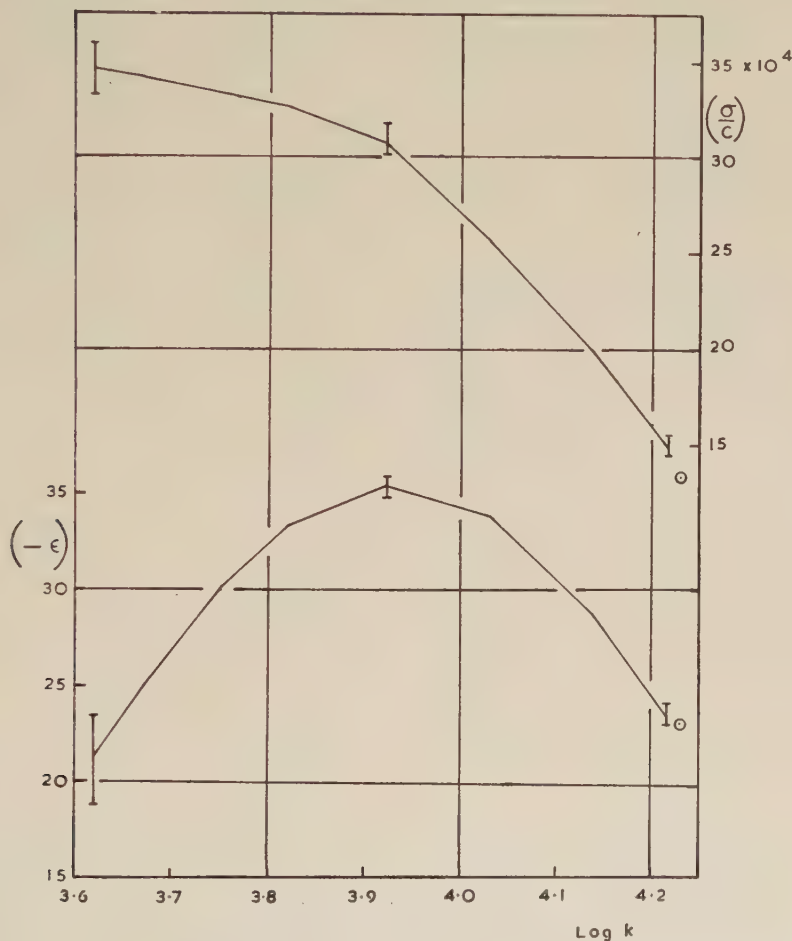
Two parameters with the dimension cm^{-1} will be useful in this discussion :

$$k_0 = \sqrt{(e^2 N / \pi m^* c^2)} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where N is the number per cm^3 of electrons with effective mass m^* . In the case when $m^* = m$, the electronic mass, (1), becomes

$$k_0 = \sqrt{(8.95 \times 10^{-14} N)}.$$

Fig. 3



Clean mercury. k = wave number in cm^{-1} , ϵ = dielectric constant, σ = conductivity in e.s.u. $\odot$ Wheeler (1911). Experimental values $-\epsilon = 3$, $\sigma/c = 24.8 \times 10^4$, for $\log k = 3.22$; Beattie and Conn (1955).

The second parameter,

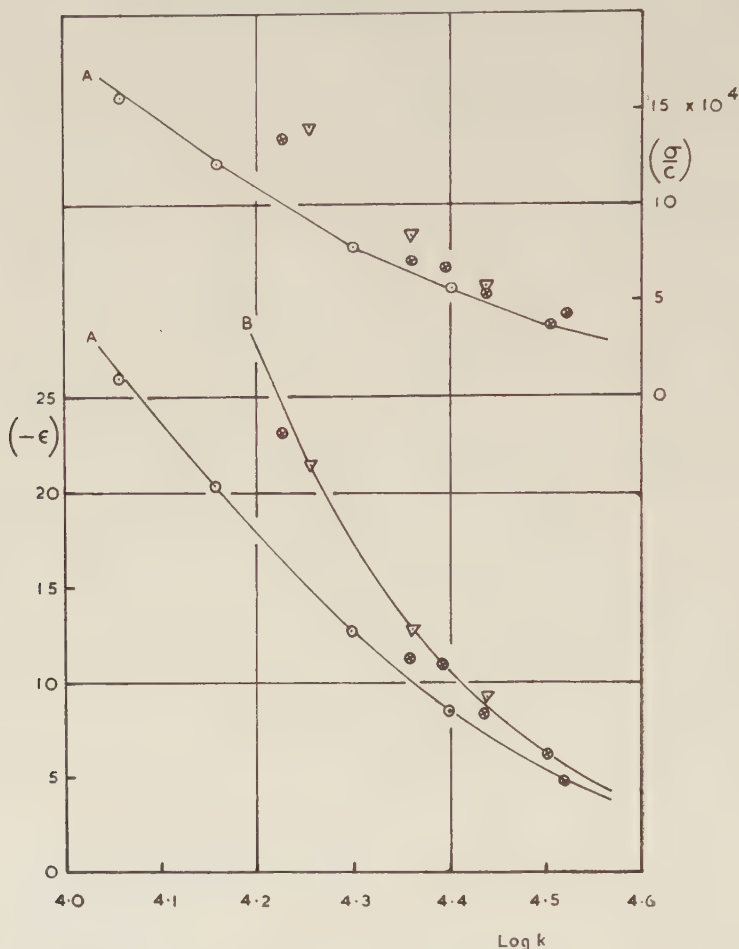
$$k_R = 2\pi / c\tau \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where τ is the relaxation time; $2\pi/\tau$ is often called γ , e.g. Seitz (1940).

The Lorentz theory for free electrons leads to

$$1 - \epsilon = \frac{k_0^2}{k^2 + k_R^2} \quad \text{and} \quad \frac{\sigma}{c} = \frac{\frac{1}{2}k_0^2 k_R}{k^2 + k_R^2} \quad \dots \quad (3)$$

Fig. 4



Mercury, visible and ultra-violet. k = wave number in cm^{-1} , ϵ = dielectric constant, σ = conductivity in e.s.u. Experimental points: $\otimes$ Wheeler (1911) and O'Brien (1926), $\circ$ Schulz (1957), ∇ Hodgson.

Curves: A: $1 - \epsilon = \frac{k_0^2}{k^2 + k_R^2}, \quad \sigma/c = \frac{\frac{1}{2}k_0^2 k_R}{k^2 + k_R^2}.$

B: $1 - \epsilon = k_0^2/k^2; \quad k_0^2 = 7.29 \times 10^9 \text{ cm}^{-2}; \quad k_R = 1.164 \times 10^4 \text{ cm}^{-1}.$

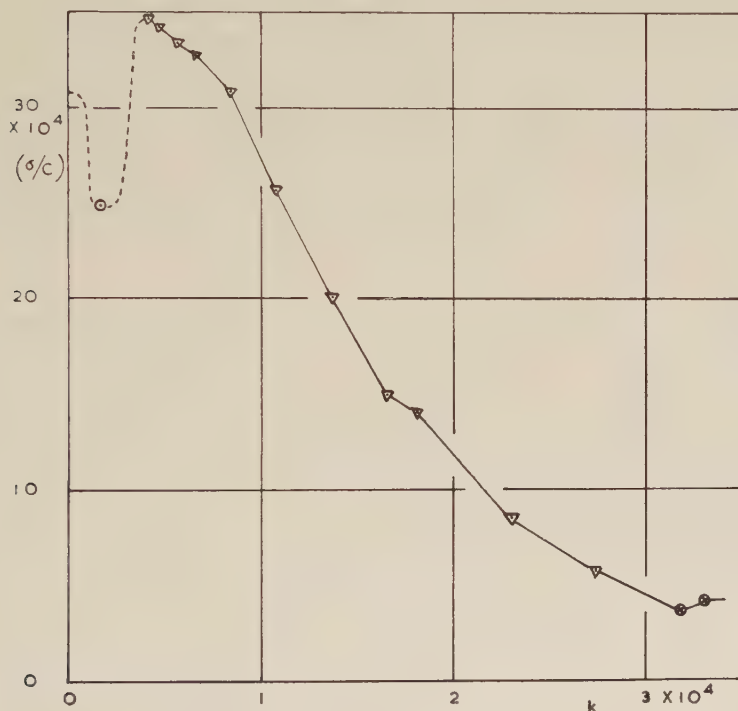
$(1 - \epsilon)$ for free electrons therefore tends to a constant value (k_0^2/k_R^2) for small k . The experimental values of $(1 - \epsilon)$ in the infra-red do not behave like this and therefore cannot be due to free electrons. The peak in $(-\epsilon)$ indicates, according to the Kramers-Kronig relations, that (σ/c) must

have a peak at smaller values of k . This is also indicated by the value of (σ/c) at $\log k = 3.22$ due to Beattie and Conn (see fig. 3). If σ_0 is the static electrical conductivity in e.s.u., then for mercury at 20°C , $(\sigma_0/c) = 31.3 \times 10^4$, compared with the maximum in (σ/c) of 34.6×10^4 .

Visible and ultra-violet values of $(-\epsilon)$ and (σ/c) are compared with theoretical curves in fig. 4. The values of Schulz agree very closely with formulae (3), taking $N/N_A = 2.0$, where N_A is the number of atoms per cm^3 , (i.e. $k_0^2 = 7.3 \times 10^9 \text{ cm}^{-2}$), and $\frac{1}{2}k_0^2/k_R = \sigma_0/c = 31.3 \times 10^4$. Schulz's measurements were made on the surface of mercury in contact with glass or silica. O'Brien's and the present values for $(-\epsilon)$, both obtained with a free mercury surface, lie close to the curve

$$1 - \epsilon = k_0^2/k^2 \quad (\text{with } k_0^2 = 7.3 \times 10^9 \text{ cm}^{-2}). \quad . \quad . \quad . \quad (4)$$

Fig. 5



Conductivity of mercury. k = wave number in cm^{-1} , σ = conductivity in e.s.u.
 Experimental points: $\circ$ Beattie and Conn (1955), $\otimes$ O'Brien (1926),
 ∇ Hodgson.

This represents the high k approximation for $N/N_A = 2.0$. A formula for ϵ should include the contribution of the ion core polarizability. An estimate of the polarizability of the Hg^{++} ion from the refractive indices of mercuric salts, led to the conclusion that the ion core contribution to ϵ is not greater than 1.0.

A curve of $\sigma(k)$ against k can be considered as the sum of curves due to electrons in each energy band. It follows from the Kramers-Kronig relations that the area under a curve of σ against k for one group of electrons, is proportional to the density of these electrons. For sufficiently large k' , the K.-K. relations give

$$\int_0^{k'} dk \frac{\sigma(k)}{c} = \frac{\pi}{4} k'^2 [1 - \epsilon(k')] = \frac{\pi}{4} k_0^2 \quad . \quad . \quad . \quad (5)$$

where σ and ϵ are the conductivity and dielectric constant due to one group of electrons. k_0 is related to the electron density by formula (1) with $m^* = m$.

The values of σ for mercury between $k=0$ and $0.4 \times 10^4 \text{ cm}^{-1}$ are not known, except for the point at $0.167 \times 10^4 \text{ cm}^{-1}$ due to Beattie and Conn. The dotted curve of fig. 5 is a possible interpolation of the experimental values. The area under the curve of σ/c shown in fig. 5, between ordinates $k=0$ and $3.4 \times 10^4 \text{ cm}^{-1}$, is $\pi/4 \times 7.3 \times 10^9 \text{ cm}^{-2}$. The value of k_0^2 for 2.0 electrons per atom in mercury is $7.3 \times 10^9 \text{ cm}^{-2}$. Therefore when $k > 3.4 \times 10^4 \text{ cm}^{-1}$ and probably for smaller k , other electrons besides the two valence electrons are making an appreciable contribution to σ . Transitions of 5d electrons to higher bands may be occurring in this spectral region. This argument depends to some extent on the interpolation shown in fig. 5, but any likely interpolation would give nearly the same total area.

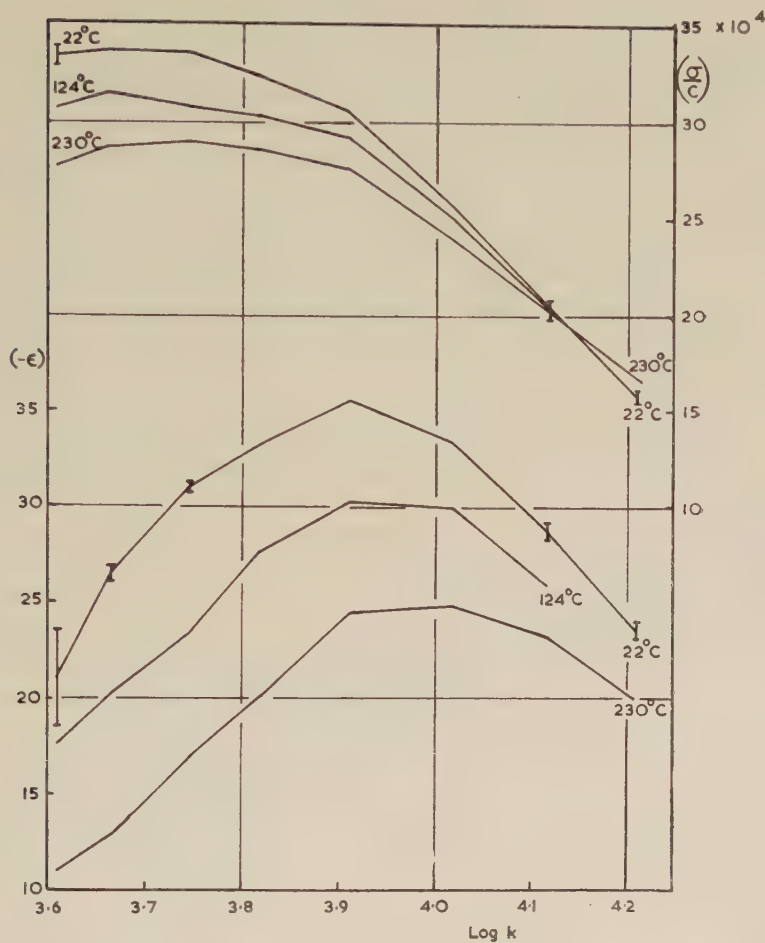
§ 7. TEMPERATURE VARIATION

The silica boat containing liquid metal can be placed inside a steel block heated by coils of nichrome wire. The temperature of the block near the silica boat is measured by a chromel-alumel thermocouple. The block can be enclosed in a water-cooled brass tank, sealed with rubber O-rings. Two windows of fused silica allow incident and reflected radiation to pass to and from the liquid metal. The windows are held by screwed flanges against rubber O-rings. Care had to be taken not to screw down the flanges too tightly because the windows are liable to strain and consequent double refraction. To ensure that the errors due to the windows are negligible, measurements were repeated using Pyrex windows.

A silica boat was filled with freshly distilled mercury and the tank was evacuated. Dry hydrogen was then passed into the tank until the pressure was a few lb/in² above atmospheric. Reflection measurements were made at room temperature, then at a higher temperature and finally again at room temperature when the mercury had cooled. Small irreversible changes in ϵ and σ occurred between the initial and final measurements. The room temperature values shown in fig. 6 are means of initial and final values and the vertical lines show the irreversible changes, where appreciable. The maximum temperature was fixed by the rate of condensation of mercury on the tank windows.

The experimental results are shown in fig. 6. The peak values of (σ/c) show a variation in the same sense as (σ_0/c) , but the ratio of values at 230°

Fig. 6



Temperature variation. k =wave number in cm^{-1} , ϵ =dielectric constant, σ =conductivity in e.s.u.

and 22°C are different; 0.860 for (σ/c) and 0.809 for (σ_0/c) . The peaks in (σ/c) and $(-\epsilon)$ move to higher k as the temperature increases.

§ 8. INDIUM-MERCURY AMALGAMS

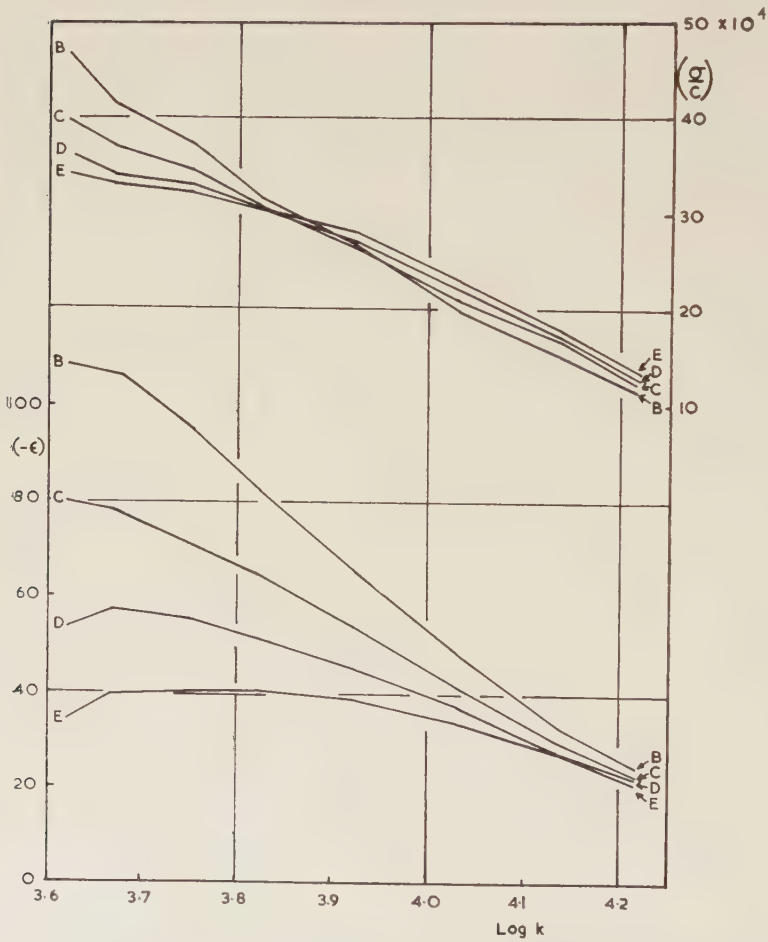
Indium is a trivalent metal with a wide range of solubility in mercury, up to 70 atm % indium. Indium amalgams B, C, D and E of varying concentrations were prepared. Some of their properties are shown in table 2. Densities were measured with a density bottle and N was calculated assuming 2.0 electrons per atom for mercury and 3.0 for indium. The amalgams were poured through a fine glass tube into a silica boat for reflection measurements. The measurements were done in air.

Table 2. Indium-Mercury Alloys

Alloy	In	B	C	D	E	Hg	
Atomic frac- tion indium	1.00	0.334	0.176	0.101	0.049	0.00	
σ_0/C	103.5†	65.1	51.6	43.5	38.1	31.3	$\times 10^4$
N	11.46		8.82	8.55	8.34	8.14	$\times 10^{22}$

σ_0 =static conductivity in e.s.u. at 20°C (Schulz 1957).
 N =number of valence electrons per cm³.
† Value for liquid In extrapolated to 20°C.

Fig. 7



Indium-mercury alloys. k =wave number in cm⁻¹, ϵ =dielectric constant,
 σ =conductivity in e.s.u.

A repeat of the measurements showed no appreciable changes in ϵ and σ after exposure to the air for 1 hour.

The experimental results are given in fig. 7. The maximum values of (σ/c) are in the same order as the values of (σ_0/c) . The peak in $(-\epsilon)$ and presumably in (σ/c) , moves to smaller k as the indium content increases.

§ 9. FUTURE MEASUREMENTS

The minimum wave number of the present measurements is just too large to show whether (σ/c) for mercury has a peak near $k=4 \times 10^3 \text{ cm}^{-1}$. The indium-mercury amalgams also probably have a peak in (σ/c) at $k < 4 \times 10^3 \text{ cm}^{-1}$. Similar measurements in the spectral region 500 to 4000 cm^{-1} are therefore planned.

ACKNOWLEDGMENT

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The Effect of Grain Size on the Tensile Properties of High-purity Molybdenum at Room Temperature†

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ABSTRACT

The room temperature yield and fracture stresses have been measured for a series of high-purity polycrystalline molybdenum tensile specimens with grain diameters varying from 0.03 mm to 0.26 mm. The yield stress results can be fitted to Petch's relation $\sigma_Y = \sigma_I + k_Y l^{-1/2}$ with $\sigma_I = 11.0 \text{ kg mm}^{-2}$ and $k_Y = 1.7 \times 10^8 \text{ dyne cm}^{-3/2}$. The fracture stress curve tends to a constant height above the yield stress curve as the grain size decreases. Using a theory of fracture recently proposed by Cottrell the effective surface energy for fracture is estimated to be $12\,000 \text{ ergs cm}^{-2}$.

§ 1. INTRODUCTION

MOST of the high melting-point metals having a body-centred cubic structure show a rapid transition from ductile to brittle behaviour as the temperature is lowered. This ductile brittle transition is preceded by a rapid increase in yield stress with decreasing temperature which occurs in a temperature range characteristic of each metal and determines the general region in which the transition occurs. The actual value of the transition temperature is influenced by many other factors such as grain size, impurity content and strain rate.

In a certain temperature range such a metal may be either ductile or brittle according to its grain size and experimental work by Petch (1953, 1954, 1956), Low (1954) and others has shown that this grain size transition can be observed in certain types of iron and steel at the temperature of liquid nitrogen. They have established that, for a given set of testing conditions, the yield stress, σ_Y , the brittle fracture stress, σ_F , and the stress for ductile cleavage fracture, $\sigma_{F'}$, are related to the average grain diameter, l , by the equations

$$\sigma_Y = \sigma_I + k_Y l^{-1/2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\sigma_F = \sigma_I + k_F l^{-1/2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and

$$\sigma_{F'} = k l^{-1/2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The parameters σ_I , k_Y , k_F and k depend on temperature, impurity content and a number of other factors.

Several theories have been formulated to explain these and other aspects of brittle behaviour. None of them is entirely satisfactory but the most

† Communicated by the Author.

promising is that due to Cottrell (1958) based on the production of micro-cracks by the association of dislocations from a pair of slip planes along their line of intersection. According to this theory, the transition grain size is determined by the relation

$$(\sigma_i d^{1/2} + k_y) k_y = \beta \mu \gamma \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and the stress for ductile cleavage fracture is related to the grain size by the equation

$$\sigma_f = \frac{\beta \mu \gamma}{k_y} d^{-1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In these two equations σ_i , σ_f and k_y are similar to σ_I , σ_F and k_Y but refer to shear stresses instead of tensile stresses. Since the tensile stress is twice the maximum shear stress, the two sets of quantities differ by a factor of two. The transition grain diameter is $2d$, β is a constant which is almost unity, μ is the rigidity modulus and γ the effective surface energy for fracture.

In the experiments described in this paper a grain size transition was observed in high-purity molybdenum at room temperature. From the yield and fracture stress results a value of γ has been calculated using Cottrell's theory. For fine grain sizes deviations from eqn. (3) were observed in which σ_F tended to a constant height above the yield stress curve as the grain diameter decreased. This effect was recently predicted by Cottrell but has not previously been observed.

§ 2. PREPARATION OF THE SPECIMENS

The starting material for the investigation was a single ingot of deoxidized arc-cast molybdenum prepared at the Armaments Research and Development Establishment, Woolwich. Its nominal impurity content is given in the table below.

Nominal Impurity Content of Arc-cast Molybdenum Ingot

Impurity	Amount present
Iron	$\sim 0.01\%$
Carbon	0.008%
Nitrogen	$\sim 0.003\%$
Silicon	$\sim 0.002\%$
Oxygen	$< 0.001\%$

Initially the ingot was 4 inches in length and 1.75 inches in diameter. By a variety of rolling and swaging operations, with suitable intermediate annealing treatments, a series of 0.25 inch diameter rods was produced covering a wide variety of grain sizes. The rods were machined into Hounsfield type tensile test pieces of 0.75 inch gauge length and 0.1 inch diameter. After polishing on a buffing wheel, the specimens were

recrystallized at 1400°C in an atmosphere of purified hydrogen to minimize the effect of the cold-worked surface layer produced by machining.

Some of the specimens are being used to study the effects of neutron irradiation on the mechanical properties of molybdenum. They had therefore to be made small because, apart from the shortage of pile space, molybdenum has a relatively high capture cross section for thermal neutrons (about 2.5 barns) and therefore causes undesirable parasitic loss of neutrons.

§ 3. EXPERIMENTAL METHOD

The tests were carried out on a modified Hounsfield tensometer. An automatic drive was provided by a fractional horse-power electric motor operating through a 500 : 1 ratio gearbox. This gave an extension rate just greater than 0.01 cm min⁻¹. On this type of tensometer the deflection of the beam operates a piston which pushes a thread of mercury from a reservoir along a capillary tube. Stress measurements are made during a test by observing the position of the mercury thread. The accuracy is probably better than 0.5% for a full-scale deflection.

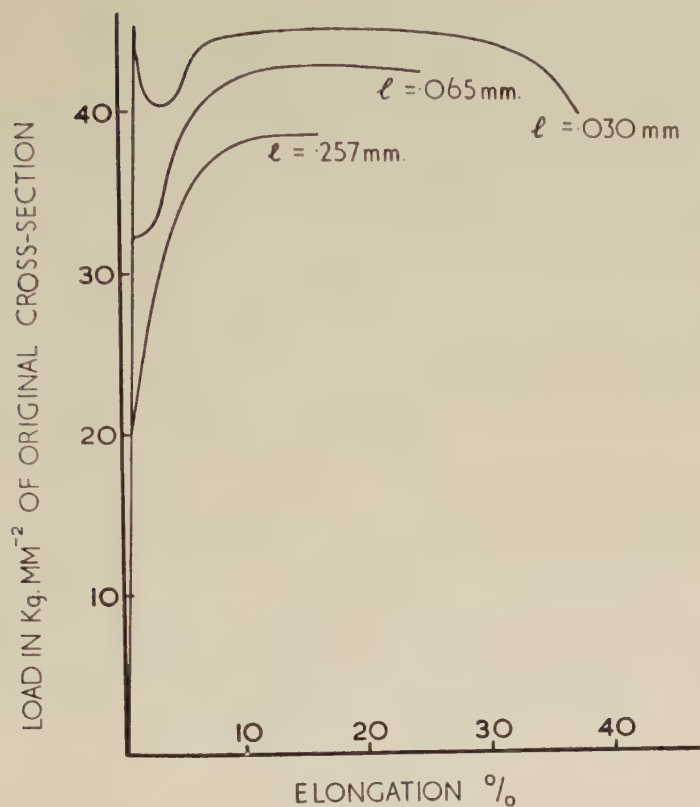
Grain size measurements were carried out on the shoulders of the specimens after they had been tested. Two methods of polishing and etching were used. In the first the specimen was mounted and polished in the usual manner and then etched in a solution made up of equal parts of hydrogen peroxide (30 vol.) and ammonia (sp. gr. 0.880). Alternatively, a simple electrolytic polish and etch similar to that described by Coons (1949) was used. Grain diameter measurements were made by the linear intercept method using a Vickers projection microscope for small grain sizes and an ordinary metallurgical microscope for the larger ones.

§ 4. RESULTS

Specimens with a fine grain size showed a pronounced yield point but as the grain size increased it systematically disappeared (fig. 1). In measuring yield stresses the stress at the lower yield point was taken when possible but otherwise the stress at which the load-elongation curve deviated from linearity was used. Figure 2 shows the yield stress plotted against the inverse square root of the grain diameter. A fairly good straight line is obtained with a positive stress intercept, σ_I of 11.0 kg mm⁻² and a gradient, k_Y of 1.7×10^8 dyne cm^{-3/2}. An almost equally good straight line can be obtained on an inverse cubed root plot and this gives a smaller positive stress intercept.

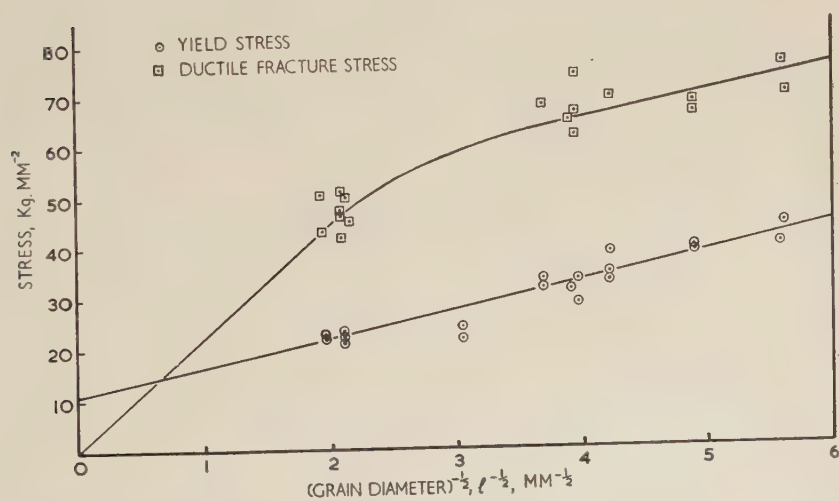
The fracture stresses cannot be fitted to an inverse square root law (fig. 2). For small grain sizes the fracture stress shows a tendency to flatten out to a constant value above the yield stress. Metallographic examination of longitudinal sections through the fracture surfaces of typical specimens showed that for large grain sizes the fracture was of the ductile cleavage type but that for fine grain sizes it was fibrous. Subsidiary cracks were observed in the vicinity of cleavage type fractures, some of

Fig. 1



The effect of grain size on the load-elongation curves of molybdenum tensile specimens at room temperature.

Fig. 2

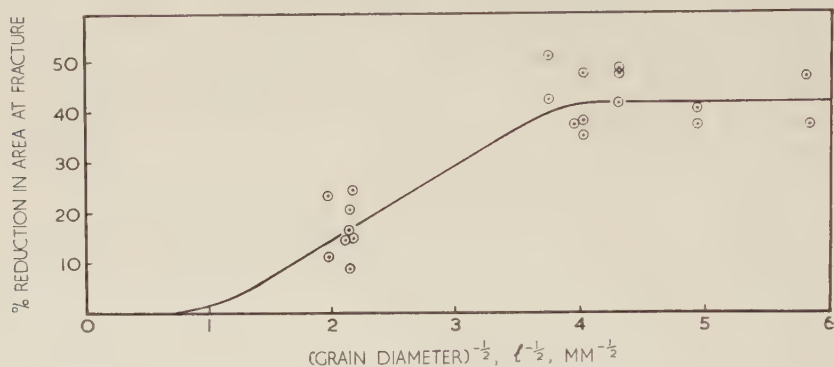


The effect of grain size on the yield and ductile fracture stresses of molybdenum tensile specimens at room temperature.

which could be seen to originate from the fracture surfaces. The reduction in area at fracture varied from about 50% for the fine grained specimens to less than 10% for those with the largest grains (fig. 3).

Two specimens with intermediate grain sizes showed anomalous fracture properties. Metallographic examination showed that they had fractured in an intercrystalline manner and their fracture results were therefore rejected. This was probably due to the absorption of oxygen or nitrogen when they were accidentally removed from the annealing furnace at too high a temperature.

Fig. 3



The effect of grain size on the percentage reduction in area at fracture of molybdenum tensile specimens at room temperature.

§ 5. DISCUSSION

The linear relation between yield stress and the inverse square root of the grain diameter is in agreement with most of the published results on other metals. Iron has a characteristically high value of σ_I which Petch has shown to be made up of a temperature-dependent part and a temperature-independent part proportional to the total carbon and nitrogen impurity content. He tentatively attributes the temperature-dependent part to the large Peierls-Nabarro force which is to be expected in a body-centred cubic metal. The relatively high value of σ_I obtained for pure molybdenum, which also has a body-centred cubic structure, would seem to support this view.

There are insufficient results to establish whether a linear relation exists between the stress for ductile cleavage fracture, σ_F , and $l^{-1/2}$ but if we assume the validity of eqn. (5) for molybdenum and join the existing group of points to the origin (fig. 1) we can calculate a value of γ from the gradient of the resulting line. Putting $\beta = 1$, $\mu = 1.2 \times 10^{12}$ dyne cm⁻² and $k_y = 6.0 \times 10^7$ dyne cm^{-3/2}, we obtain $\gamma = 12\,000$ ergs cm⁻². This compares with a value of 8000 ergs cm⁻² obtained by Cottrell (1958) as a result of a rather uncertain calculation made by taking values of σ_Y and l at the ductile-brittle transition temperature from some results of Bechtold (1954) and a value of k_Y from the results of Carreker and Guard (1956). Inserting our value of γ into eqn. (4) and putting $\sigma_i = 5.4 \times 10^8$ dyne cm⁻²

the transition grain diameter comes out to be 2.2 mm. All the specimens tested showed some deformation before fracture but a plausible extrapolation to zero reduction in area of the curve relation reduction in area at fracture to grain size gives a result close to this value (fig. 3). This extrapolation is based on the shape of analogous curves for iron.

The tendency for the fracture stress curve to flatten out to a constant height above the yield stress curve for small grain sizes is believed to be due to a fracture mode transition in which the type of fracture changes from ductile cleavage to fibrous as the grain size decreases. In the first type cleavage occurs after a limited amount of work hardening but in the second it is supposed that fracture occurs by the failure of the material bridging the many microcracks created during plastic deformation. This fracture mode transition is well known but the relation between the yield and fracture stresses for very ductile material, although predicted by Cottrell, has not previously been observed.

ACKNOWLEDGMENTS

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Observations on Single Crystals of an Isotactic Polyolefin: Morphology and Chain Packing in Poly-4-Methyl-Pentene-1†

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ABSTRACT

Single crystals of isotactic poly-4-methyl pentene-1 were prepared from solution. The crystals were mostly flat squares with more or less regular shapes. They consisted of thin square layers forming spiral terraces centred on screw dislocations. The molecules were found to be perpendicular to these layers. The same polymer could also be obtained in the form of thin fibrils with the molecules perpendicular to the fibril direction. Both these habits require chain folding, further implications of which are discussed.

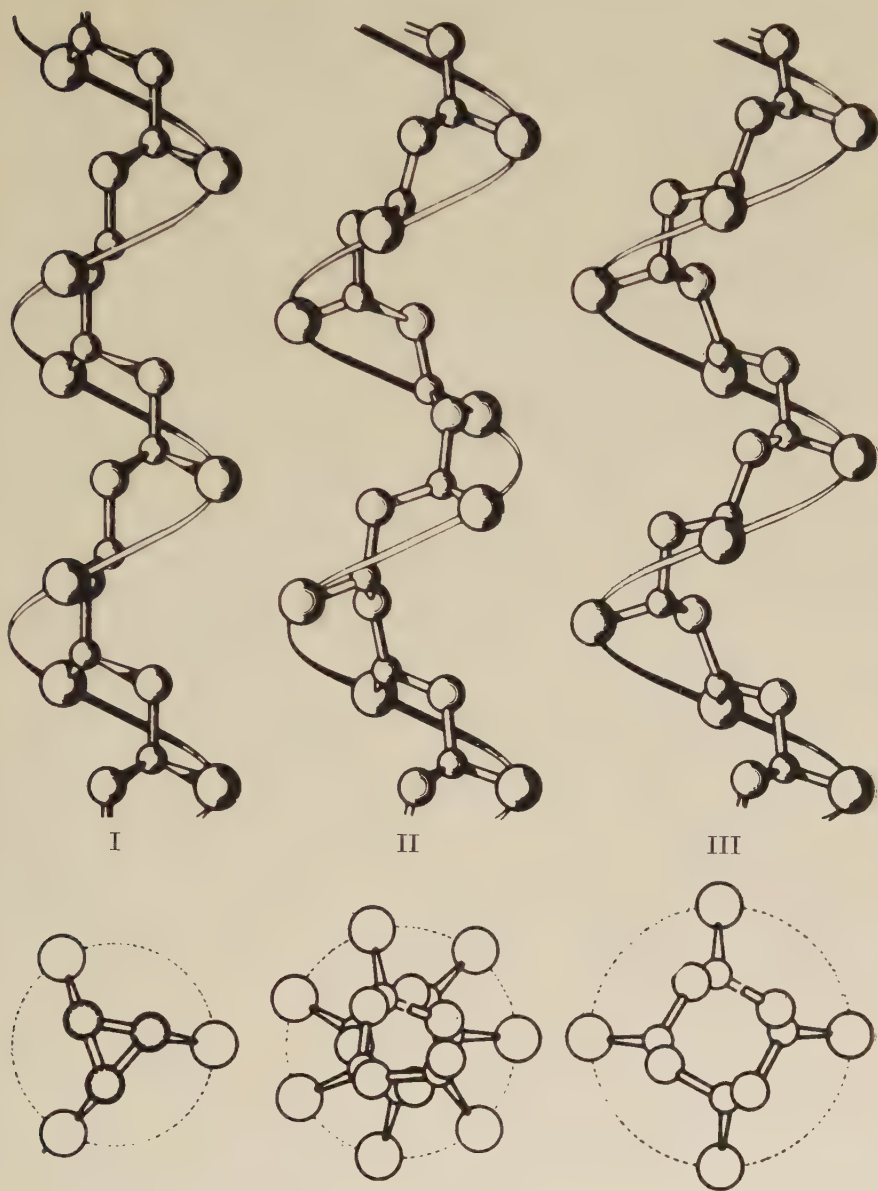
The unit cell was determined and was found to be tetragonal with $a=b=18.66$ Å and $c=13.80$ Å containing four chains. The packing of these chains closely approximates a two-dimensional rock-salt type arrangement with one chain surrounded by four nearest neighbours. It is shown that the helical chains can be in gear with this type of packing, engaging most perfectly if half and half are of opposite winding direction.

§ 1. INTRODUCTION

It has been shown recently (Keller 1957, Till 1957, Fischer 1957) that linear polyethylenes can be obtained in the form of single crystals with paraffin-type habits. The crystals consisted of layers approximately 100 Å thick, thickening through spiral terraces centred on screw dislocations. The long chain molecules were found to be perpendicular to these layers. It was postulated (Keller 1957) that the molecules must be sharply folded at regular intervals in order to be accommodated by these thin layers. Low angle x-ray reflections (Keller and O'Connor 1957) could be identified with this layering and with the corresponding fold period. As the bounding faces of the crystals were of the {110} type it was postulated that these planes might contain the folds (Keller and O'Connor 1958). This would require the existence of four different quadrants within the crystal. The existence of distinguishable quadrants which are at least consistent with this suggestion have in fact been lately revealed (Agar *et al.* 1959, also referred to in Keller and O'Connor 1958). Further, polyamides were crystallized in fibrillar form (Keller 1958) and it was shown that against all expectations the molecules were nearly perpendicular to the length of the microfibrils. As the fibrils are thinner than the molecules are long this again requires a folded molecular configuration.

† Communicated by the Authors.

Fig. 1



- I : $R = -CH_3, -C_2H_5, -CH=CH_2, -CH_2CH_2CH(CH_3)_2, -OCH_3, -OCH_2CH(CH_3)_2, -C_6H_5.$
 II : $R = -CH_2CH(CH_3)C_2H_5, -CH_2CH(CH_3)_2.$
 III : $R = -CH(CH_3)_2, -C_2H_5.$

Chain configurations of isotactic polyolefins (after Natta).
 Poly-4-methyl-pentene-1 belongs to group II.

The material of our present investigations was the isotactic poly-4-methyl-pentene-1 ($-\text{CH}_2-\text{CH}[\text{CH}_2-\text{CH}-(\text{CH}_3)_2]-$)_n, i.e. a polymethylene chain with a $-\text{CH}_2-\text{CH}-(\text{CH}_3)_2$ group on every second carbon atom along the chain. The 'isotactic' synthesis (Natta 1955, Natta *et al.* 1955a) ensures that the side groups are sterically all in the same orientation, i.e. they are either all in a right-handed or all in a left-handed position with respect to the carbon atom in the chain. Because of this regularity of the side groups, isotactic polymers can all be obtained in crystalline form in contrast to the so-called atactic polymers where the steric positions of the side groups are in an irregular sequence.

The following information was available when the present work was started. The simple polymethylene chain in the usual paraffins and polyethylenes takes up a planar zig-zag configuration in the crystal. This corresponds to the chain carbon atoms being in staggered trans positions (see e.g. Bunn and Holmes 1958). The side groups in the isotactic polyolefins, however, may not permit such a planar configuration owing to steric interference. By introducing also gauche positions the distance between these side groups can be increased, but then the chain will become a helix. The steepness of the helix depends on the side group. Figure 1 shows three helices with three, three and a half and four monomer units per turn. Poly-4-methyl-pentene-1 belongs to group II with seven units per two turns. The unit cell and also the structure has been determined for several substances belonging to group I, but to our knowledge only the cell dimension along the chain has been identified for some of the others. In the case of poly-4-methyl-pentene-1, Natta *et al.* (1955b) found a repeat period of 13.85 Å along the chain which agrees well with the figure expected from the steric considerations in fig. 1. The only other x-ray data available (Natta *et al.* 1955b) give the following three equatorial reflections corresponding to the lateral packing of the chains: 9.31 Å strong, 6.61 Å medium and 4.15 Å medium strong. The x-ray melting point was given as 200–205°C, and density as 0.831 (Natta *et al.* 1955c).

§ 2. EXPERIMENTAL

The poly-4-methyl-pentene-1 was received in powder form, from M. Gordon, Arthur D. Little Research Institute, Inveresk, where the substance was prepared by L. D. Loan, and the following data were available: Viscometrically determined molecular weight was found to be of the order of 10^5 as distinct from 10^4 or 10^6 . The density of the solid was 0.847 at 17.5°C (Natta *et al.* 1955c, give a density of 0.831). The partial specific volume in dilute benzene solution at 67.5°C was 1.217 and in decalin at 96.5°C, 1.228. The melting point determined by ourselves visually was 202–206°C in good agreement with the data obtained from x-ray observation by Natta, Corradini and Bassi (1955b).

For the purpose of our investigations the powder was dissolved in hot xylene and crystallized in the form of a suspension by lowering the temperature of the solution. We found that conditions were not as

reproducible as with the similar experiments on polyethylene, and the appearance of the crystals depended rather unpredictably on the rate of cooling. Most of our preparations were obtained by immersing a test tube containing a few millilitres of the dilute solution (0.01% to 0.1%) in a 100–200 ml oil bath heated previously to about 120°C. The bath was then allowed to cool to room temperature in the usual laboratory environment. After a few days the suspension was sedimented on to a carbon-coated glass slide and could be directly examined either under the optical microscope, usually in phase contrast illumination, or after floating off the carbon film, under the electron microscope in direct transmission.

It was found that the precipitate could be obtained in the form of single crystals with well-defined faces. In the case of the most regular development these crystals consisted of square shaped layers as in fig. 5 (Pl. 36). The thickness of the layers, as assessed from the shadows, was about 90–150 Å. These layers were seen to form spiral terraces. Figure 6 (Pl. 40) shows a clear example of one double spiral near the centre of a crystal. In fig. 7 (Pl. 37) two adjacent spirals of opposite sense can be seen in the lower half of the crystal. In figs. 5, 6 and 7 superposed layers on the upper and lower surfaces of the crystals can be distinguished, the latter pushing through and making steps on the top, shadowed, surface which are visibly less sharp than those surrounding the former, and more diffuse the greater the thickness of overlying crystal. Some of the small superposed layers, of which examples are seen in fig. 5 (Pl. 36) are D-shaped, with one particularly straight side. The reason for this is not known. Frequently a main layer has a distinct shallow outward-facing step near its periphery, so that there is a border a little thinner than the rest of the crystal. Screw dislocations with associated thickening growth are particularly common in these border regions.

Some of these crystals were heat-treated by placing the glass slide on a hot surface. If in this process the melting point ($\sim 203^{\circ}\text{C}$) was just about reached, the appearance of the crystal changed, to form characteristic patterns (fig. 8, Pl. 37). One consistent feature appearing in such heated crystals was the concentration of matter along the diagonals of the squares.

One preparation gave picture-frame type crystals (fig. 9, Pl. 40). These frames could be seen usually singly or occasionally in pairs. Occasionally two or more could be superposed. Electron micrographs (fig. 10, Pl. 38) revealed that the frames consisted of piled up layers about 100 Å thick each, while electron diffraction revealed that the frames were not empty but consisted of a single layer in the centre.

The most frequently observed habit was of the type shown by fig. 11 (Pl. 39). It can be seen that these, at first sight irregular aggregates, are in fact malformed squares. Deviation from the square shape often arose through a characteristic rounding-off at the corners. In some cases at least this was seen to be due to a doubling back of the layers at the corners, although this in itself would not directly account for the

curvature. The square shape was frequently marred by incipient dendrite formation and by fibrillation. Except for places where this fibrillation occurred, the crystals consisted of flat layers. In the thicker interior opaque lines were apparent which in many cases appeared to consist of folded or rolled-up layers. Occasionally they might have been layers standing edge on. Usually these thickenings formed irregular polygons or circles concentric with the crystal boundaries, but we also have electron micrographs where they form well-defined squares at 45° to the crystals.

The electron diffraction patterns were recorded by using the electron microscope as a diffraction instrument. Fast working was essential and special precautions were needed as the patterns rapidly faded and vanished under the effect of the electron beam (Keller 1958). All the above crystals gave clearly defined diffraction spots. When individual squares or parts of squares were selected with the selecting aperture, patterns as in fig. 12 (Pl. 40) were obtained with the beam in normal incidence. The planes corresponding to the strongest spots were parallel to the faces of the crystals. The rings in the illustration were due to the shadowing metal coating and correspond to spacings of 2.34 and 2.12 Å. The calibration was carried out more accurately by evaporating a thin layer of TiCl_2 on the specimen, and by using the 100 TiCl_2 lines at 3.834 Å as standards (Boswell 1950). In this way the strongest reflections in fig. 12 (Pl. 40) were found to correspond to 9.27–32 Å, the higher values in this range being more probable owing to the particular shape of the line profile.

When the suspension was filtered slowly the sedimenting crystals formed a coherent film resembling the one obtained under similar circumstances with polyethylene (Keller and O'Connor 1957). These films could be examined by x-rays. When the beam was perpendicular to the film plane the pattern consisted of continuous rings, but when it was parallel to the film an oriented pattern as shown by fig. 13 (Pl. 40) was obtained. This indicates a fibre symmetry around the film normal. The strongest innermost equatorial arc corresponded to ~ 9.3 Å and is identical with the strongest reflection in the electron diffraction pattern of fig. 12 (Pl. 40). This in itself suggests that the crystals all sedimented approximately horizontally. The appreciable spread of the reflections in fig. 13 (Pl. 40) is to be expected, as the top surfaces of the crystals are not even. The reflection marked with the arrow (to be referred to later) was measured as 5.3 Å. On oscillating around an axis perpendicular to the fibre direction (vertical in fig. 13, Pl. 40) an appreciably strong reflection appeared at 1.93 Å perpendicular to the axis of oscillation. Low-angle x-ray photographs of such films gave one weak but sharply defined reflection at a Bragg spacing of 108 Å corresponding to planes parallel to the film plane.

All the previous preparations were obtained from xylene. From a trichlorethylene solution evaporated on a slide after cooling, dendritic

shapes could be observed under the optical microscope. It was established that these crystals did not grow within the liquid on cooling but formed while the solvent was evaporating, at least when the solutions were prepared on the same day. The electron micrographs revealed that these apparent dendrites were in fact rows of parallel sheaves consisting of fibrils about 100–200Å thick (fig. 14, Pl. 41). These sheaves were reminiscent of the aggregates familiar from studies on spherulitic growth (Keller and Waring 1955). Sometimes the assembly consisted essentially of rows of parallel fibrils (fig. 15, Pl. 41), presumably because the nucleation occurred at close intervals, preventing an appreciable divergence of the fibrils. A periodicity of about 200Å was noticeable along the fibrils. Electron diffraction patterns of such rows of fibrils or sheaves (fig. 16, Pl. 40) gave two pairs of arced reflections, one at 9.3Å and another at 5.30Å. The arcs are seen to be in the same orientation relative to each other, as in fig. 13 (Pl. 40), the direction of the fibril bisecting the 9.3Å arcs. The 5.3Å reflection, weaker than in fig. 13 (Pl. 40), is a broad diffuse arc about the row direction, i.e. the direction normal to the fibrils.

§ 3. DISCUSSION

3.1. Morphological Features and Chain Folding

According to the experimental findings isotactic poly-4-methyl-pentene-1 forms single crystals consisting of thin layers. The spiral terrace arrangement of such layers is familiar from crystal growth studies and corresponds to growth initiated by screw dislocations. This mode of crystallization is analogous to that of paraffins and linear polyethylenes, apart from the square shape. In the case of most regular development there was one spiral pyramid, hence one dislocation in the centre of the crystals. Frequently, however, a number of these were present, particularly at the edges of the terraces. A probable partial interpretation of the picture-frame crystals is that these were formed from single layers with slightly *thinner* borders, such as can be observed; that a rather large number of screw dislocations were produced in these borders, causing them to thicken in the usual manner by forming spiral terraces. Thickening within the interior in the form of folds or rolls is again analogous to similar effects in polyethylene lozenges, where they are believed to represent the initial stages of spherulitic growth accounting for the correct orientation within the spherulites. This might also be the case in poly-4-methyl-pentene-1, but without information about spherulites in this material the analogy cannot be made more concrete at the present stage.

Figures 14 and 15 (Pl. 41) show that this polymer can also crystallize in fibrillar form. This fibrillar habit also appears in parts of the preparations consisting of square crystals (fig. 11, Pl. 39). Prior to the discovery of polyethylene lozenges it was thought that high polymers crystallize with a fibrillar or ribbon-like habit. Recent work on polyamides (Keller 1958) provides further evidence for this fibrillar or ribbon-like

habit, while there is an accumulation of evidence that polyethylenes nearly always form layer-shaped crystals. Consequently it is of particular interest that poly-4-methyl-pentene-1 could be obtained in both of these habits. In a particular polymer one or the other mode may be more prominent under the usual conditions of crystallization.

Electron-diffraction patterns confirmed in the first place that the square or near square-shaped objects were single crystals. The pattern revealed four-fold symmetry in agreement with the observed square habit. The square cell dimension is around $18.6\text{\AA}$ (the most conspicuous layer lines are in fact halved by weak spots which may not be visible in the reproduction), and the indices of the strongest $9.3\text{\AA}$ reflections are $\{200\}$. The next strongest ones in fig. 12 (Pl. 40) are $\{220\}$ and $\{420\}$ with spacings 6.6 and $4.15\text{\AA}$ respectively. Thus we have indexed the reflections listed as equatorial by Natta *et al.* (1955 b) (see introduction). The same reflections were also identified as equatorial in the x-ray pattern of fig. 13 (Pl. 40). The $1.93\text{\AA}$ reflection obtained on tilting the film giving fig. 13 (Pl. 40) corresponds to the (007) reflection (Natta *et al.* 1955 b) which identifies fig. 13 (Pl. 40) with a diffraction pattern given by a drawn fibre, with the molecules along the fibre axis (we did not possess drawn fibres for this work). As these films were formed through a parallel piling up of flat square crystals, fig. 12 (Pl. 40) corresponds to a pattern with the molecules parallel to the beam, a fact which is *a priori* obvious from the high symmetry of the pattern. Consequently we conclude that the molecules are perpendicular to the crystal layers.

The finding that long molecules are perpendicular to the surface of thin layers, much thinner than the molecules are long, is analogous to the one encountered in polyethylenes. Clearly the molecules cannot be exactly perpendicular and stay straight. As in the case of polyethylene, we postulate that they must fold sharply back on themselves without disturbing the packing of the chains. Thus the layer thickness and also the strength of the screw dislocations would correspond to the fold period. With polyethylene this periodicity was also reflected by the four orders of a large meridional spacing in x-ray diffraction patterns analogous to fig. 13 (Pl. 40). There is evidence for the same in poly-4-methyl-pentene-1 but the low-angle reflection, while sharp, appears only in one order and has a low intensity. Though this low-angle x-ray evidence in itself is less conclusive than in the case of polyethylene, there is no reason to doubt that we are dealing with the same phenomenon, the difference being due to the inherently lower intensity of the diffraction effects at small angles.

As shown by fig. 16 (Pl. 40), there are two strong $\{200\}$ arcs, ($9.3\text{\AA}$ spacing) meridional with respect to the fibrils of figs. 14 and 15. Thus $[100]$ axes lie along the fibrils. It follows that the long axes of the molecules (i.e. the axes of the helices which they form), being $[001]$, as is further confirmed below, lie transverse to the fibrils. This is a situation, still a little surprising, which we come to recognize as customary in the

crystallization of long chains. It is precisely analogous to the situation in the fibrillar crystals of polyamides (Keller 1958). The molecular length is much greater than the width of the fibrils, and the molecules must therefore fold within the fibrils, as in the layer crystals, and must do so rather regularly to make fibrils of apparently uniform width.

The only other prominent reflection in fig. 16 is a pair of wide equatorial arcs at a spacing of $5.3\text{\AA}$. This, which we index (below) as 212, is also prominent in fig. 13 (Pl. 40). Its position and intensity relative to 200 is consistent with a simple fibre orientation, with $[100]$ as fibre axis along the fibrils: this, with perfectly parallel fibrils, would give 212 spots at about 55° from the meridian. However, there is only a very weak 200 reflection near the equator, so there cannot be full fibre symmetry—the chain axes, $[001]$, must be preferentially non-normal to the substrate. A fuller texture determination with a specimen which so readily loses crystallinity in the electron beam would be difficult to carry out. It follows from all these conclusions that in some respect polymers are similar to both the tabular paraffin crystals and to the fibrous greases, where the long but not polymeric molecules lie across the layers or fibrils respectively.

Folding was an unexpected phenomenon even when first recognized in polyethylenes. While it could be demonstrated that the required folding is sterically possible (Keller and O'Connor 1958), the exact regularity of the fold periods is still largely unaccounted for. It is still more unexpected that a bulky chain such as poly-4-methyl-pentene-1 with relatively large side groups, should behave in this way. While no doubt the bulkier chain might not be able to fold as sharply, this should be allowed for by the larger intermolecular distance available for this folding. The fact that the chain itself is helical need not represent an obstacle since there is no need for it to maintain the helix within the fold.

It was argued in connection with polyethylene (Keller and O'Connor 1958) that the crystal faces are expected to contain the plane of the folds. Accordingly in poly-4-methyl-pentene-1 the chains would be expected to fold in the (100) and (010) planes in different parts of the square crystals. This again requires the existence of four structurally distinguishable quadrants with boundaries along the square diagonals. In fact some structural significance of these diagonals has become apparent in the crystals heated to the melting point (fig. 8, Pl. 37). While the causes of this effect are not understood it is an indication of some discontinuity along these lines which at least is consistent with the above assumption.

3.2. *Some Comments on the Packing of the Chains*

The square crystal, and the four-fold symmetry of the diffraction pattern obtained with the beam normal to it, indicates a tetragonal structure, which is confirmed by the possibility of indexing all reflections in an x-ray powder photograph on the basis of a tetragonal cell with $a = 18.66\text{\AA}$, $c = 13.80\text{\AA}$. The correspondence of the single crystal and sedimented film diffraction results with those of Natta *et al.* (1955 b) for drawn fibres

indicates that the chains are in the c -axis direction. The cell dimensions, and the significant 007 reflection support Natta's assignment of a helical configuration (of type II in fig. 1) for the chains, and could not well be accounted for otherwise. The density requires four molecules per cell, the theoretical density thus calculated being 0.813. This is in good agreement with the specific volume measurements in dilute solution, but is somewhat lower than the value obtained by direct measurements on the solid. While this latter discrepancy is unaccountable at present, it does not affect the principal conclusion of four chains occupying one cell.

In the following the packing of the chains will be defined more closely on the basis of the $hk0$ reflections in fig. 12 (Pl. 40). These reflections are listed in table 1.

Table 1

Index	Spacing (Å)	Intensity
100		} masked by primary beam
110		
200	9.3	
210	8.35	
220	6.6	v.s.
300	—	v.w.
310	—	s.
320	—	—
400	4.65	—
410	4.5	w.
330	—	v.w.
420	4.15	—
430	3.12	m.s.
500	—	v.v.w.
510	—	—
520	—	—
440	3.3	—
530	—	v.w.
600	3.1	—
		limit of detection

In order to place four chains in a tetragonal cell at least one tetrad or four-fold inversion axis is required per cell and the molecules must be related through this symmetry element. By placing these tetrad or four-fold inversion axes at the corners of the cell, we can define the structure as consisting of clusters of four chains around each cell corner. The relative displacement of the chains along their length will not affect the $hk0$ reflections, consequently all configurations with chains differing in their z coordinates only will be equivalent for the present discussion. Thus we may choose $z=0$.

If all the chains are identical the arrangement of four molecules around each cell corner corresponds to space group $P4$ for the general positions

of the chains. If pairs of chains are related by inversion, we have space group $P\bar{4}$. An inversion relation will exist if one-half of the helices (fig. 1) has a different winding direction from that of the other half. Helices of opposite sense are known to exist in those polyolefins where the structure has been more closely determined (e.g. Natta *et al.* 1956). For this, and also for reasons to become clear later, we shall refer to two kinds of helices in the deductions to follow, although the arguments should be equally valid for the case where all the helices are of one kind only.

A general configuration is shown by fig. 2. It will be seen that the chains define two kinds of squares, one kind being at the cell corners, the other at the cell centre. In general these two kinds of squares are unequal both in size and in orientation. If we denote the coordinates of a given chain by x and y , the squares will be of equal size, if $x + y = \frac{1}{2}$, and they will be in the same orientation if $x - y = 0$. If both these conditions are satisfied we have the arrangement shown by fig. 3. Here all chains are in identical environment, and if the helices are of two kinds, those of the one kind will be surrounded by four nearest neighbours of the other. This is a two-dimensional equivalent of the rock salt structure. (Naturally in the case of fig. 3, a smaller unit cell can be defined containing two molecules only.)

The structure factor for either $P\bar{4}$ or $P\bar{4}$ (fig. 2), and for $hk0$ reflections, is

$$F = 4 \cos \pi[(h-k)x + (h+k)y] \cos \pi[(h+k)x - (h-k)y]$$

which may also be written as

$$F = 4 \cos (h\alpha - k\beta) \cos (h\beta + k\alpha) \quad . \quad . \quad . \quad (1)$$

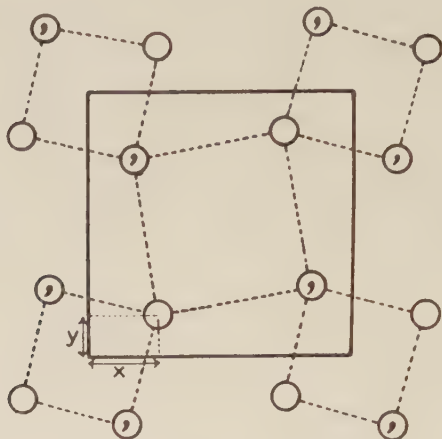
by introducing new parameters

$$\alpha = \pi(x + y), \quad \beta = \pi(x - y).$$

If $\alpha = \pi/2$ and $\beta = 0$ (corresponding to fig. 3), then if either of the indices h or k is odd one of the factors in F is zero, and if both are odd, both factors in F are zero. Table 1 shows that in fact reflections with one odd index are either very weak or absent, while those with two odd indices are absent. This indicates that the structure approximates closely, but not exactly, to fig. 3. The alternation of intensities with odd and even indices continues at least as far as 600, the highest order seen. If either α or β differed from $\pi/2$ or 0, respectively, by as much as $\pi/12$, this alternation would reverse at the sixth order. Since there is no sign of an approaching reversal, we infer that the deviation from the structure of fig. 3, cannot be more than, say, 0.2 in either of the parameters α or β . F should in general be unequal for reflections $hk0$ and $kh0$, unless one of the equalities, $\alpha = \pi/2$ or $\beta = 0$, is exact. There is no visible difference in intensity between such reflections, so that we have grounds to infer that the departure from the structure is in one of the parameters only (i.e. the squares are either equal or parallel). However, the small asymmetry if this were not the

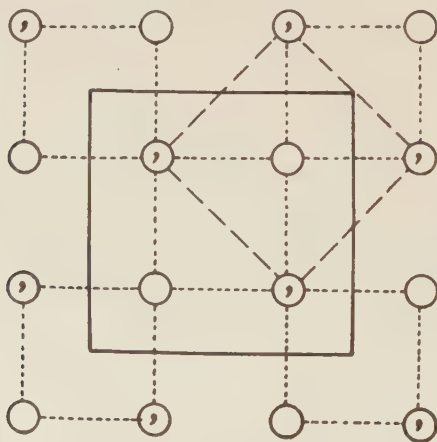
case would be very likely to lead to twinning, which would make no change in the shape of the crystal, and would remove the asymmetry from the diffraction diagram: so that this conclusion is not wholly reliable.

Fig. 2



The most general arrangement of four chains in a tetragonal unit cell. The circles represent the chains. As drawn, those with , within them are related by inversion to those without this sign, corresponding to helices of opposite winding direction. In this case there is a four-fold inversion axis at each cell corner, the cell edges being drawn solid. The two kinds of squares (see text) are outlined dotted.

Fig. 3



The arrangement in fig. 2 in the special case when $x+y=\frac{1}{2}$ and $x-y=0$. In this case the actual unit cell is smaller as shown by the interrupted line.

Next, one may ask for the reason of the four-fold symmetry. Smooth cylinders are expected to pack hexagonally. The same would apply to screwed rods but in this case closest packing requires that the screws

should all be of the same kind. Clearly, deviation from hexagonal symmetry must be due in the first place to the presence of side groups. We represent the seven groups per repeat unit (two turns) as dots along a circle in fig. 4. These can be divided most evenly into four by forming three sectors with two, and one with one group. Figure 4 shows seven helices forming the two kinds of squares mentioned above. The squares centred on cell corners and cell edges are now different. One contains one side group per helix in each repeat distance and the other two. This would make $\alpha \neq \pi/2$ but allow $\beta = 0$. However, by a small rotation we can make the helices present similar faces towards the cell corners and centres, and dissimilar faces towards the centres of the cell edges, leading to $\beta \neq 0$ but allowing $\alpha = \pi/2$. In fact, the incompatibility of the seven-fold (screw) axis of a helix with a four-fold symmetry of environment explains why $(\alpha - \pi/2)$ and β should not be simultaneously zero, but does not tell us in which of the parameters the deviation should occur, or exclude its occurrence in both.

Above we considered the side groups as lying along a circle. In fact they follow a helix. Consider now this helix as a continuous screwed rod. For best packing the ridges of one helix will have to fit into the grooves of the nearest neighbour. This may be described as a phase difference of π at the contact. In fig. 4 the phases of the helices at each contact with a neighbour are marked relative to an arbitrary zero, taking adjacent helices as right and left handed (marked by R and L respectively in the figure). We assume that $\beta = 0$, i.e. the squares are all parallel. It is seen that all nearest neighbours are in gear. The screw threads also run parallel to each other where in contact. If the helices were all of the same kind the same phase relations would hold at the points of contact but the threads would cross, making for less perfect packing. If β were not equal to zero, so that the neighbours of a helix were not all 90° apart, the perfect 'phase' relation of ridges and grooves could not be everywhere maintained. If the phase error was uniformly distributed among the contacts it would amount to approximately $4\beta/\pi$: i.e. an error of $2\beta/\pi^2$ when expressed as a fraction of the screw pitch. These considerations make it plausible that the structure is likely to be $P\bar{4}$ (with right and left-handed helices) rather than $P4$ (with all of one kind) and that β , rather than $(\alpha - \pi/2)$, is zero or very small. Provisionally acceptable parameters for the structure are $x=y \sim 0.27$.

The main cause for the adoption of this structure by the material must be considered to be the severe incompatibility of the seven-fold symmetry of the helices with six-fold coordination. A five-fold coordination of cylinders exists ($P4$ or $P\bar{4}$ with a larger value of β than we can accept for this case) which would be relatively advantageous in this regard, but particularly bad for the engagement of the screw threads. The four-fold coordination gives the closest cylinder packing which satisfies both requirements for the protrusions.

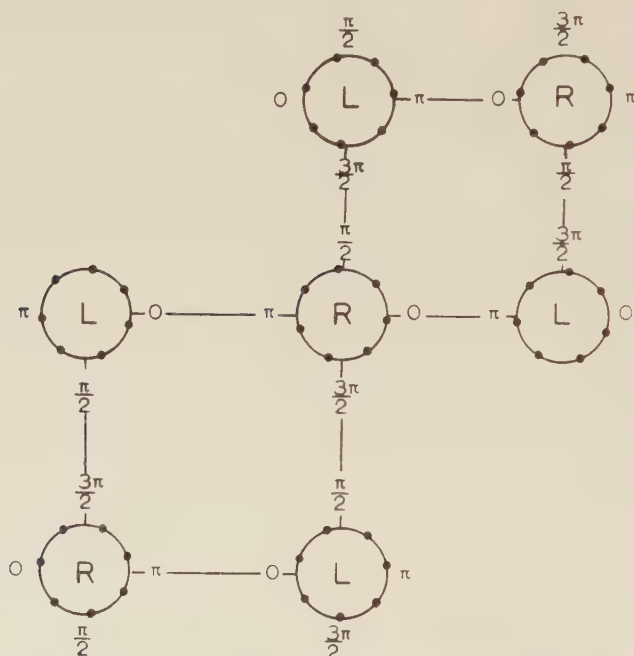
It will be noted from table 1 that reflections around the radius of 3-4 reciprocal units are either absent (in the case where any index is odd)

or are unexpectedly weak as for 400. The fact that these absences or weakenings are in a circular zone points to the effect of the molecular scattering factor. The Fourier transform of a uniform cylinder in the $hk0$ plane is

$$T(\rho) = \frac{v}{\rho} J_1(2\pi\rho r) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where ρ is the radial coordinate in reciprocal space, r is the radius of the cylinder and J_1 the Bessel function of first order. By putting $r = \frac{1}{4}$, i.e. by taking the diameter of a cylinder as half of the unit cell width, we get the first zero for T at 2.4 reciprocal units. This is less than the observed radius of weakening at ~ 3.5 . This discrepancy indicates that the assumption of a uniform cylinder is not fulfilled, and that the charge density

Fig. 4



The packing of seven chains forming two kinds of square (see text). The squares are drawn in identical orientations ($x-y=0$). The circles represent the helices in projection, and the seven dots along them the seven side groups per repeat unit. R and L denote right and left-handed helices respectively and the phase of the windings with respect to an arbitrarily chosen 0 are denoted along four directions around each chain.

(electron or proton for x-ray or electron scattering respectively) is higher at the core than at the periphery. This can be readily verified as follows. We consider the methylene chain as contained by a solid cylinder of radius r' , and the side groups by a surrounding cylindrical annulus of radii r' and r . By taking $r = 0.25$ as before, and $r' = 0.096$ (corresponding

to 3.5Å) we find that the average charge density within the core is 2.7 times higher than within the surrounding shell. Regarding this density as uniformly distributed within these regions we obtain the molecular scattering factor by forming the transform of the larger cylinder with radius r weighted by the lower charge density (taken as unity) and adding to this the transform of the smaller cylinder of radius r' weighted by the density difference between the two cylinders (1.7). With the insertion of these numerical factors the transform is

$$T(\rho) = \frac{1}{\rho} \left[0.25 J_1 \left(\frac{\pi}{2} \rho \right) + 0.177 J_1 \left(\frac{\pi}{5.3} \rho \right) \right]. \quad (3)$$

This expression has a sharp minimum at 3.5Å in agreement with the observed radius of the zone of weakening in the electron diffraction pattern.

Table 2

Index	Calc. spacing Å	Obs. spacing Å	Intensity
101	11.090	11.130	w.
200	9.330	9.263	v.s.
210	8.345	8.441	w.
201	7.727	7.798	w.
211	7.139	7.246	w.
220	6.597	6.602	m.s.
301	5.689	5.746	w.
311	5.425	5.389	s.
212	5.315	5.281	s.
320	5.176	—	v.v.w.
321	4.846	4.854	s.
400	4.666	4.666	w.
312	4.483	4.538	w.
401	4.419	4.424	w.
411	4.300	4.292	m.s.
331 } 420 }	4.188 } 4.173 }	4.167	m.s.
412	3.784	3.770	w.
422	3.571	3.567	v.w.
440	3.298	3.283	v.w.

Finally we list in table 2 the indices spacings and intensities of a number of reflections obtained from powder photographs for possible further work on the structure. The photographs were obtained with monochromatic radiation in vacuo on unoriented specimens in a Guinier focusing camera. Calibration was carried out with reference to the 100 TiCl_2 line taken as 3.834Å (Boswell 1950). The a and c values were obtained by a graphical method employing all the observed reflections, giving unit cell dimensions: $a = b = 18.66\text{Å}$ and $c = 13.80\text{Å}$. There is a slight difference between the x-ray and electron diffraction figures for the a spacing. We consider our x-ray determination as the more accurate one.

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Nucleon Clusters in the Nuclear Surface†

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ABSTRACT

The absorption of slow K^- -meson by complex nuclei frequently results in the emission of fast $\Sigma^\pm$ -hyperons unaccompanied by π -mesons. This observation is combined with the argument of Jones that such absorption is a surface phenomenon to suggest that the nuclear surface is rich in nucleon clusters, possibly 'alpha-particles'.

THE region of low density in the nuclear surface is not well investigated experimentally but there are signs that it is relatively rich in nucleon clusters such as alpha-particles. This is at first sight surprising but such condensation is energetically encouraged and is not inhibited by the Pauli principle when the density is low.

The evidence is chiefly: (i) that calculations of absolute alpha-particle emission rates in the heavy elements agree with experiment only on the assumption of a large measure of 'pre-formation' of the alpha-particles in the nuclear surface (see e.g. Perlman and Rasmussen 1957); (ii) that alpha-particle reduced widths in the lighter elements are substantial fractions of a single particle unit (Wilkinson 1958); (iii) that 'direct interaction' production of alpha-particles in reactions such as (p, α) requires a substantial number of preformed 'target' alpha-particles in the nuclear surface (Hodgson 1958).

We have less present information about other forms of surface cluster and almost none about nucleon-nucleon correlations (high momentum states) as such, specifically in the tenuous region. Such high momentum states (greater than the 250 mev/c appropriate to a single nucleon of the Fermi-sea) should be found in the surface if nucleon clusters are probable there but not if the tailing off of the nuclear density is due chiefly to single nucleons. This note is to point out that evidence is available from the capture of slow K^- -mesons by nuclei in nuclear emulsion that high momentum states are indeed rather common in the nuclear surface.

It was shown by Jones (1958) that, owing to their strong interaction with nucleons, K^- -mesons which have been brought to rest in matter will spiral towards the nucleus of the capturing atom and be captured into it from a high Bohr orbit—typically 5g in a nucleus of medium weight such as the silver or bromine of nuclear emulsion. For an imaginary potential of about 100 mev such as is indicated by the available data on

† Communicated by the Author.

K^- -meson-nucleon and K^- -meson-nucleus interactions and for a Stanford matter distribution the probability of capture has its maximum about 2.0 fermis further out than the point at which the nuclear density has fallen to a half of its central value. 80% of the capture is on the outermost 10% of the nuclear matter. The probability of absorption within the radius at which the nuclear density has 90% of its central value, which is generally taken to limit the surface region, is less than 1%.

These numbers are little changed by the introduction of 10 to 20 mev of real K^- -meson-nucleus potential, attractive or repulsive. They must of course be somewhat sensitive to the form of the tail of the matter distribution but this has not been well investigated. The absorption of K^- -mesons by the light elements of nuclear emulsion is even more a surface phenomenon. The general validity of Jones' picture of surface absorption was demonstrated by Chadwick *et al.* (1958); it has recently received further support (Kaplon 1958)†. These considerations, as Jones pointed out, make the K^- -meson a potentially very valuable tool for studying specifically the composition of the nuclear surface. If the tenuous surface in which the K^- -mesons are absorbed consists chiefly of single nucleons then the hyperons which are produced will come from the pion producing reactions: nucleon + $K^- = Y + \pi$. With the help of a Fermi momentum of 250 mev/c for the capturing nucleon the $\Sigma^\pm$ -hyperon energy will range up to about 60 mev. But if in the nuclear surface there exist nucleon clusters then in addition to this first form of reaction the higher momentum states that these clusters afford will enable reactions such as: $pp + K^- = \Sigma^+ + n$ to take place (the momentum here is 500 mev/c)‡. Such a reaction would yield over 100 mev to the hyperon in free space and over 160 mev to the hyperon for a reasonable laboratory momentum of the high momentum state as a whole of 220 mev/c. In practice (see e.g. Kaplon 1958) slow K^- -meson absorption in nuclear emulsion yields slow $\Sigma^\pm$ -hyperons (below 60 mev) accompanied by π -mesons but also a substantial number of fast $\Sigma^\pm$ -hyperons of energy greater than 60 mev. These latter are not accompanied by π -mesons and are the result of absorption into the high momentum components of nucleon clusters. 15% and possibly 30% of all slow K^- -meson absorptions go through this high momentum mechanism and so it seems that nucleon clusters account for a large proportion of the nucleons in the nuclear surface. This conclusion could be wrong if the effective cross section of a nucleon pair for absorbing a K^- -meson were much bigger than that of a single nucleon. This is unlikely to be so because the K^- -meson-nucleon cross section for

† The experimental evidence, which is of several kinds, argues against a very large real attractive part for the K^- -meson-nucleus potential which is the only thing which could reasonably falsify Jones' prediction.

‡ We shall not explicitly discuss the absorption into three or more nucleons that are simultaneously correlated. These processes will contribute to the fast hyperon yield but are likely to be relatively unimportant compared with the two-nucleon correlations.

$\Sigma^\pm$ -hyperon production is already large—20 to 50 mb for K^- -mesons of a few mev†. We also note that about one-half of the fast charged hyperons are Σ^+ ; these can come only from two strongly interacting protons; the other half, the Σ^- can come from np or nn states. At least it is clear that surface 'deuteron' clusters alone would not suffice. Such loose clusters would in any case not readily result in fast hyperon emission; it is reported by Tripp (1958) that possibly about 1% of slow K^- -meson absorptions in deuterium are non-mesonic. The size of the surface cluster will influence the probability of absorption into a high momentum state. We should consider clusters of 2, 3 and 4 nucleons. A measure of the characteristic size of these clusters, at least in the free state, that is directly available for the deuteron and He^4 , is the root mean square radius of the nucleon distribution. On this there is evidence from high energy electron scattering (see e.g. Ravenhall 1958) and photodisintegration (Rustgi and Levinger 1957, Foldy 1957) which gives the rms radius of the charge distribution. When this is corrected for the rms radius of the proton (0.77 fermi) we find rms radii for the nucleon distribution of 1.95 and 1.38 fermis respectively for D and He^4 . No such evaluation is possible for H^3 and He^3 but we may use the successful theoretical treatment of Kikuta *et al.* (1956) to deduce a corresponding nucleon rms radius of 1.46 fermis. The number of nucleon pairings per unit volume then stands in the ratio of 1 : 7 : 17 for D : H^3 , He^3 : He^4 . These figures are, of course, extremely crude but they indicate that the observed fast hyperon production may be consistent with the observed yield from deuterium for an absorption on alpha-particle clusters. Clusters of mass 3 are less likely candidates because of their lower pair density, because of their greater ratio of Σ^- to Σ^+ -hyperon producing pairs and because their binding energy to the rest of the nucleus is much greater‡.

Another approach has been made by Chadwick (1958) who applies to the present problem the treatment given by Ruderman and Karplus (1956) for discussing the ratio of non-mesonic to mesonic hyper-fragment decay

† Another conceivable but unreasonable circumstance is that all surface nucleons exist in clusters and that clustering inhibits K^- -meson absorption so that the absorption takes place within the body of the nucleus. This would leave the conclusions of this note unchanged but invalidate the argument leading to them. This possibility is countered by the fact that the cross section for absorption of K^- -mesons in flight is considerably larger than the geometrical.

‡ Of course we cannot imagine that these surface clusters which are continually dissolving and reforming bear close resemblance to the corresponding cluster in the free state. It is conceivable that for example the two nucleon cluster in the nuclear surface is sufficiently richer in high momentum components than the free deuteron to explain the observed fast hyperon yield. The present discussion in which surface clusters are awarded the names of familiar particles is only intended to show the consistency of this simplest way of looking at the situation. The experiments of themselves do no more than demonstrate the presence of nucleon-nucleon correlations in the nuclear surface.

by regarding the absorption of the K^- -meson as producing a virtual hyperon. Straightforward use of the Ruderman-Karplus argument then suggests that the K^- -meson must be absorbed in nuclear matter of approximately the normal saturation density (such as is the case for an alpha-particle) in order to explain the large yield of fast hyperons.

It seems indeed that the experimental results are consistent with *all* slow K^- -meson absorption taking place in surface clusters, possibly 'alpha-particles'. It is interesting that Hodgson's (1958) conclusion, based on a study of (p, α) reactions in nuclear emulsion, was that a surface nucleon in silver or bromine spends about 0.4 of its time in an alpha-particle. This is in complete accord with the present suggestion.

We summarize: Since the arguments of Jones have shown that stopped K^- -mesons are absorbed in the surface region of low *mean* nucleon density, the abundant production of fast $\Sigma^\pm$ -hyperons from such absorptions show that high momentum states that we must associate with nucleon clusters are common in this region. Further very tentative considerations show that these clusters are possibly 'alpha-particles'.

Experiments on the direct absorption of K^- -mesons in helium will obviously be of great interest in this connection. If they show a non-mesonic yield of 15 to 30% we must probably conclude that alpha-particles are the rule rather than the exception in the nuclear surface. If the non-mesonic yield is much greater than 30%, which seems very unlikely, we have evidence for some K^- -meson absorption in complex nuclei on single nucleons in their own right rather than as constituent but low-momentum members of clusters (we postpone a discussion of the surface of the surface cluster). If the non-mesonic yield from helium is very low our understanding of the mechanism of K^- -meson interactions in complex nuclei is faulty.

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On the Low Temperature Optical Absorption of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}^\dagger$

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ABSTRACT

The optical absorption of crystals of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ was studied at room temperature, 90°K and 20°K . Some peculiarities in these spectra are reported and discussed. A tentative assignment of the observed transitions to levels predicted in terms of crystal field theory is made, obtaining a satisfactory agreement, if an appropriate set of parameters is used.

§ 1. INTRODUCTION

THE validity of the ligand field theory (Ilse and Hartmann 1951, Abragam and Pryce 1951 a, b, Orgel 1952, Tanabe and Sugano 1954) as a powerful means to interpret the absorption spectra of iron group elements, seems by now fairly well established after extensive work on the optical absorption of solutions and crystals (for a comprehensive collection of references, see Jørgensen 1956).

The physical model used in this theory—namely, a central paramagnetic ion, whose electrons are responsible for the absorption, surrounded by ligands schematized as point charges or dipoles—has proved a remarkably good approximation for the case of solutions.

Assuming a ligand field of cubic symmetry, as a first approximation, many of the electronic levels calculated present orbital and spin degeneracy. The former is very probably lifted, as indicated by the observed structure in many absorptions (Gielesse 1935, Bjerrum *et al.* 1954, Holmes and McClure 1957), by many mechanisms such as non-cubic components of the field, either static or arising from the Jahn–Teller effect (due to vibrations of the complex ion) and finally by spin–orbit coupling.

A detailed theoretical calculation of the splitting of these degenerate levels is in general hampered by inadequate knowledge of too many physical parameters.

In the case of Co^{2+} the ground state is a ${}^4\text{T}_1({}^4\text{F})$ state with threefold orbital degeneracy. As early as 1951 Abragam and Pryce calculated the

[†] Communicated by Professor M. H. L. Pryce, F.R.S. This research was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command.

set of levels arising from ${}^4T_1$, for the case of trigonal and tetragonal field symmetries including the effect of spin-orbit coupling.

Hexahydrated cobaltous chloride and bromide absorption spectra show lines, or narrow bands, with characteristic temperature dependence, which can perhaps be correlated with ground levels arising from ${}^4T_1({}^4F)$.

Other interesting properties of the absorption of these salts are: (a) the presence at 20°K of remarkably sharp lines, sharper, e.g. than the mercury are lines; (b) the position of the main absorption band in the visible is shifted more than 1000 cm^{-1} towards lower frequencies by comparison with the analogous band in cobalt chloride aqueous solutions and with the corresponding band in crystals of $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (unpublished results) and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (Holmes and McClure 1957).

This last property would point to a strong crystalline† field effect in cobalt halide hexahydrates.

§ 2. THE EXPERIMENTAL APPARATUS

For details of the experimental set-up, see *Phil. Mag.*, 1957, 2, 1397. Since we were mainly interested in absorption lines, a photographic method of detection was used.

The spectra were taken with a large Hilger quartz spectrograph and with a Hilger medium spectrograph, equipped with glass optics for better resolution in the red region of the spectrum.

Ilford Rapid Process Pancromatic and Kodak Scientific IM and IIL Plates were used; the plates were scanned with a Leeds and Northrup recording densitometer.

Absorption spectra were taken at room temperature, 90°K and 20°K (also 78°K for the chloride). The investigated region ranged from $\sim 11\,000$ to $27\,000\text{ cm}^{-1}$. The crystalline samples had thicknesses of $0.8 \sim 0.9\text{ mm}$ and were obtained by recrystallization of analytically pure reagents. Absorption spectra in the infra-red and visible region were also taken at room temperature with a Beckman quartz spectrophotometer using crystals $\sim 0.2\text{ mm}$ thick. However, observation of structure in the absorptions is more difficult by this method.

2.1. Intensity Determinations

Two different methods of intensity determination were used for strong and weak absorptions; of course, the intensity values reported are not claimed to be precise, in view of the well-known limitations of the photographic method.

For weak lines the procedure was the following: from the densitometric tracing the background density, in the absence of absorption, and that of the absorption peak were determined. Then a curve $d = d(t)$ (t exposure

† Crystalline field is used here as a term with a more restricted meaning than ligand field, which applies both to the liquid and solid state.

time, d plate density) was plotted for the peak of the absorption line. For an exposure time t_1 , the peak density corresponds to an incident energy $E_1 = I_\nu t_1$, that of the background to $E_0 = I_0 t_1$. If the line is weak ($I_0 \sim I_\nu$) the density corresponding to E_0 can be derived from the plotted curve as a $I_\nu \cdot (t_1 + \Delta t)$. Since $I_0 \sim I_\nu$ we are justified in assuming the validity of the Roscoë-Bunsen law, so that equal densities correspond to equal incident energies and $I_0 t_1 = I_\nu (t_1 + \Delta t)$ [where Δt is obtained from the plotted $d = d(t)$].

For stronger lines failure of the reciprocity law is taken into account by plotting on logarithmic paper $d = d(t)$ for the peak of the line and for near-by background, so as to minimize variations in plate sensitivity. If the obtained curves are similar, that is, if they can be superposed with a translation parallel to the abscissae axis, then their separation gives $\log I_0/I_\nu$. This method is less useful for strong broad absorptions, especially if situated in regions in which the sensitivity of the plate varies remarkably.

The first method is only affected by uncertainty on the value of the background.

2.2. Frequency Measurements

A comparator did not prove very useful. On the contrary frequency determinations were obtained from densitometric curves by comparison with a template calibrated in terms of the mercury arc spectrum, superposed on each absorption spectrum.

We estimate the maximum uncertainty in the absolute wave-numbers, as due to possible non-linear vertical movement of the plate-holder both in the spectrograph and in the densitometer, and to other causes of error, to be less than 100 cm^{-1} in the $15\,000 \text{ cm}^{-1}$ region and less than 70 cm^{-1} in the $25\,000 \text{ cm}^{-1}$ region. This uncertainty is further reduced in the case of sharp lines, where it is possible to measure more accurately, with optical methods, the distance from reference mercury lines.

Of course, differences of wave-number values are in general more accurate. The oscillator strength was calculated using relation (3.1) in Tanabe and Sugano (1954). The plotted extinction coefficient is that contained in the usual relation $I = I_0 10^{-\alpha x}$ (x in cm).

§ 3. THE OPTICAL ABSORPTION: EXPERIMENTAL RESULTS

The main features of the low temperature absorption in both salts are: an intense band centred at $\sim 18\,500 \text{ cm}^{-1}$ and resolved into two peaks of similar intensity; narrow lines in the $19\,000$ – $21\,000 \text{ cm}^{-1}$ region; some sort of weak broad absorption in the $21\,500$ – $245\,000 \text{ cm}^{-1}$ region, showing some structure at low temperature; finally, in this same region, and up to $26\,000 \text{ cm}^{-1}$ narrow weak lines in both salts.

The reported curves which follow give the various values of plate density. In view of the considerations of the preceding paragraph on

intensity measurements, no immediate deduction on actual absorption values can be drawn from these curves without knowing $d = d(t)$.

3.1. Cobalt Chloride†

At room temperature the absorption spectrum consists of (table 1) a main band in the yellow region of the spectrum, showing the beginning of resolution into two peaks at 18 500 and 18 800 cm^{-1} (fig. 1). On the high-frequency side of the band are a couple of broad lines (figs. 1, 2) which are centred at 19 700 cm^{-1} , followed by a narrow rather intense band. The lines have a separation of $\sim 100 \text{ cm}^{-1}$ and the peak of the narrow

Table 1. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ at Room Temperature

Absorpt. peaks and lines	Wave-number (cm^{-1})	Half-width (cm^{-1})	Relative intensity	Extinc. coeff. $\alpha_{\text{max}}(\text{cm}^{-1})$	Oscillator strength
$A_1^\dagger$	18420	~ 3000		~ 22	9.5×10^{-5}
$A_2^\dagger$	18730				
B_0'	19640	130	0.19	2.6	4.5×10^{-7}
B_0''	19760	110	0.18	1.9	2.8×10^{-7}
B	20050	210	1	10	$3 \cdot 10^{-6}$
$C^\ddagger$	20380	1000		1.9	2.5×10^{-6}
	20730				
$E^\S$	21800				
$E_{ }$	25050				

† Peaks of main band (see fig. 1).

‡ Shoulders of band centred at 20 050 cm^{-1} (fig. 3).

§ Peak of 21 250–22 800 cm^{-1} continuous absorption (fig. 3).

|| Flat broad line.

band is at 20 050 cm^{-1} . Two shoulders of the latter appear at 20 380 and 20 730 cm^{-1} . Finally, a weak band ranging from 21 250 to 22 800 cm^{-1} , with peak at 21 800 cm^{-1} (fig. 3). Using a Beckman spectrophotometer the half-width and extinction coefficient of the main band at 18 500 are found to be respectively $\sim 3000 \text{ cm}^{-1}$ and $\alpha \sim 22$. With the same method the infra-red band is found to be centred at $8.0 \times 10^3 \text{ cm}^{-1}$.

At 90°K the splitting of the principal band is now well evident, with peaks at 18 400 and 18 900 cm^{-1} , the second stronger than the first (table 2, fig. 4(a)).

The group of lines at 20 000 cm^{-1} undergoes a remarkable modification: a very weak line is present at 19 850, the former broad line at 20 050 is now centred at 20 190 and shows a pronounced splitting into two

† In what follows we shall mean by cobalt chloride (or bromide) the hexahydrated salt of divalent cobalt.

components (B_1 and B_2) of comparable intensity, situated at 20 130 and 20 250 cm^{-1} (table 2, fig. 4(a), (b)).

Then follows a weak diffuse line at 20 405, a weaker one at 20 610, and a narrow band at 20 850 cm^{-1} (fig. 4(a), (b)). The former weak band

Fig. 1

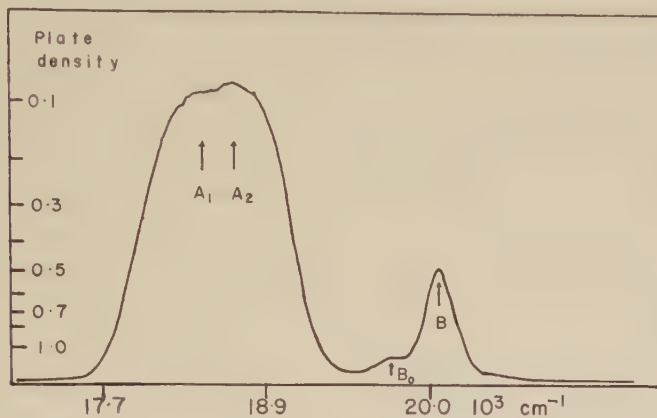
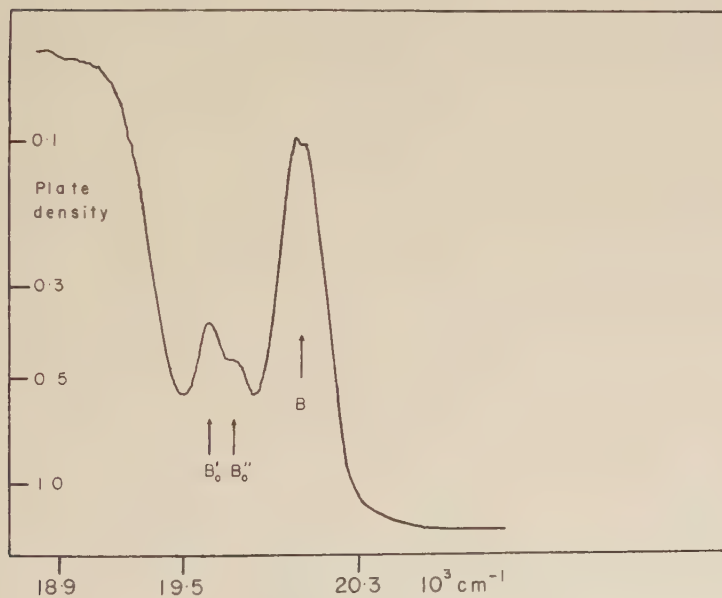
Absorption bands of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ at room temperature

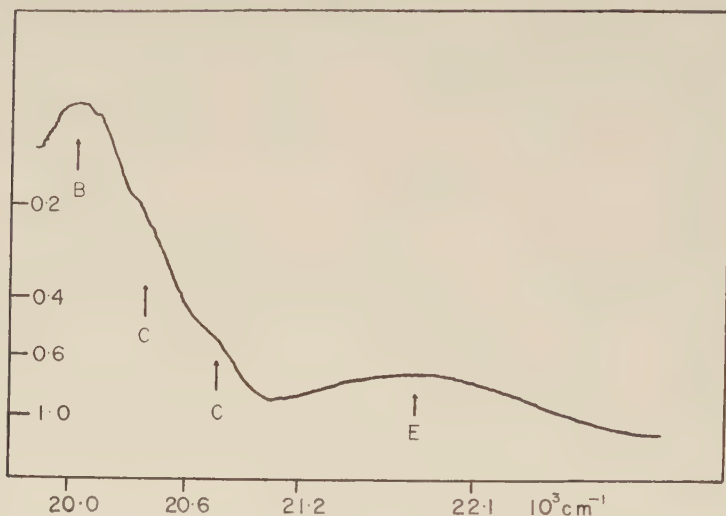
Fig. 2

Detail of the absorption of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ at room temperature.

ranging from 21 250 to 22 800 shows now some structure at 21 500 and 22 140 cm^{-1} . There is some evidence of weak diffuse lines in the 27 000 cm^{-1} region,

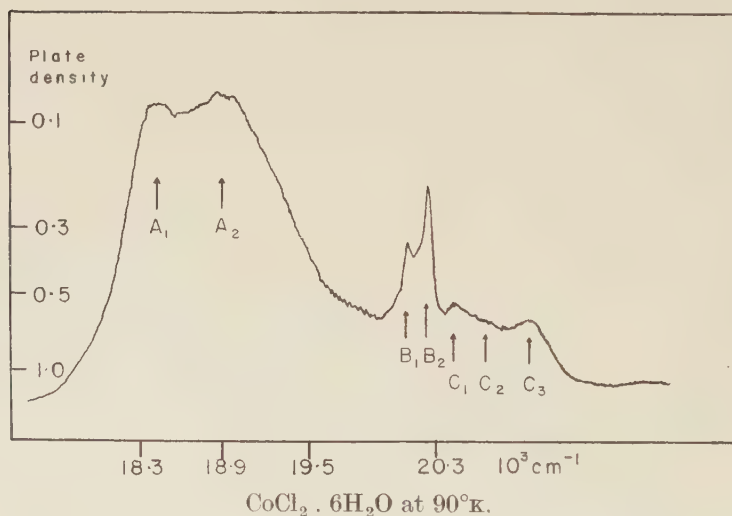
At 78°K the new features of the absorption are the following: the doublet B_1 , B_2 (fig. 5(a)) following a weak sharp line at $19\,850\text{ cm}^{-1}$ registers a sensible decrease of its low-frequency component, that now appears as a shoulder of the stronger component.

Fig. 3



$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ at room temperature ($20\,000\text{--}22\,000\text{ cm}^{-1}$ region).

Fig. 4(a)



In the $25\,000\text{ cm}^{-1}$ region weak lines now appear at $24\,840$, $25\,030$ and $25\,420\text{ cm}^{-1}$.

At 20°K the low-frequency side of the main band now presents a possible shoulder at $17\,800\text{ cm}^{-1}$,

Table 2. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ at 90°K

Absorpt. peaks and lines	Wave-number (cm^{-1})	Half-width (cm^{-1})	Relative intensity	Extinc. coeff. $\alpha_{\text{max}}(\text{cm}^{-1})$	Oscillator strength
$A_1^\dagger$	18400		0.85		
$A_2^\dagger$	18900		1		
B_0	19850				
B_1	20130	90	0.55	4	5×10^{-7}
B_2	20250	100	1	6.8	9.2×10^{-7}
C_1	20405			2	
$C_2^\ddagger$	20610				
C_3	20850			3	
	21500			1.65	
	21850(?)				
$E\S$	22140			3.3	
	22890(?)				
	23390				
	24100				
$E_{1 }$	24700				
	24880(?)				
F	26320				

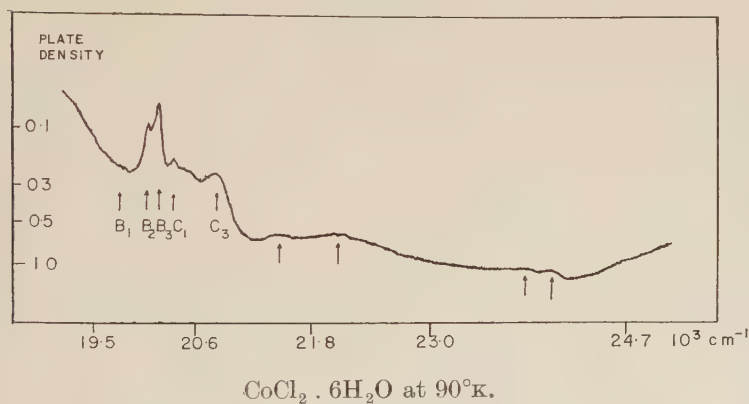
† Peaks of main band (fig. 4(a)).

‡ Very weak.

$\S$ Structure of broad weak absorption (21 400–24 300 cm^{-1}) (fig. 4(b)).

$||$ Weak narrow bands.

Fig. 4(b)



The peaks of the main band (fig. 6(a)) are now located at 18 370 and 18 900 cm^{-1} . No appreciable shift is to be found in the relative separation of the two peaks; only, as a probable effect of the 'freezing' of lattice vibrations in the ground state, the dip between the two peaks is enhanced and there is indication of fine structure in the contour of the band. As

for line groups B, C, D (fig. 6 (a), (b)), doublet B is now located at 20 175 and 20 260 cm^{-1} , that is, no appreciable frequency shift is observed from 90°K downwards for the stronger component. The same can be said for the C and D absorptions at 20 420, 20 620 and 20 880; their intensity is not remarkably changed and only a sharpening is observed in them.

Fig. 5 (a)

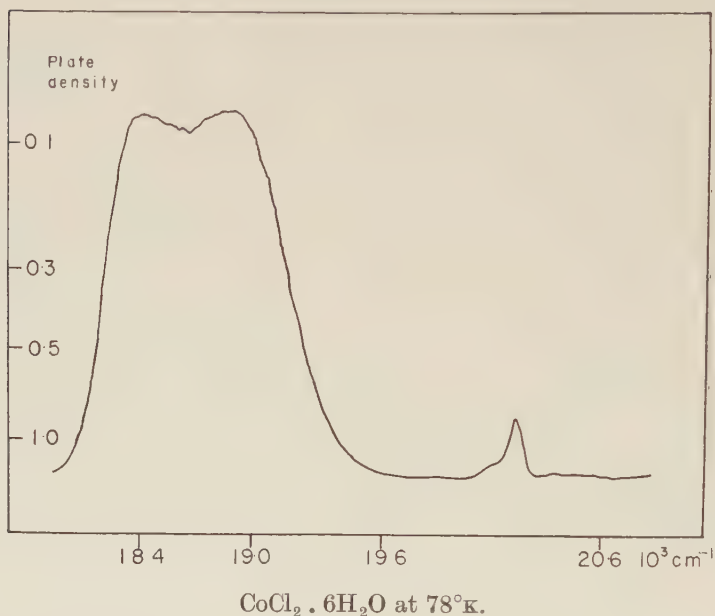
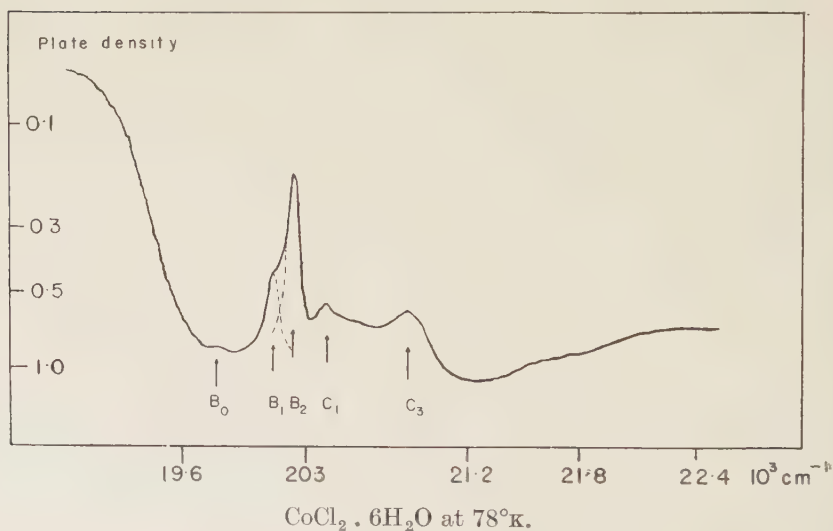


Fig. 5 (b)



On the other hand, a strong change is noticed in the intensity of the B doublet: the intensity of the second component is now preponderant. Since B_1 is now simply a shoulder, it is not easy to determine the separation of the two components: so that while the distance (fig. 6 (b)) between the peak and the shoulder is 45 cm^{-1} , resolving the composite line into two gaussians, we estimate the separation of the two peaks as $\sim 85 \text{ cm}^{-1}$, that is less, anyhow, than the separation at 90°K .

Fig. 6 (a)

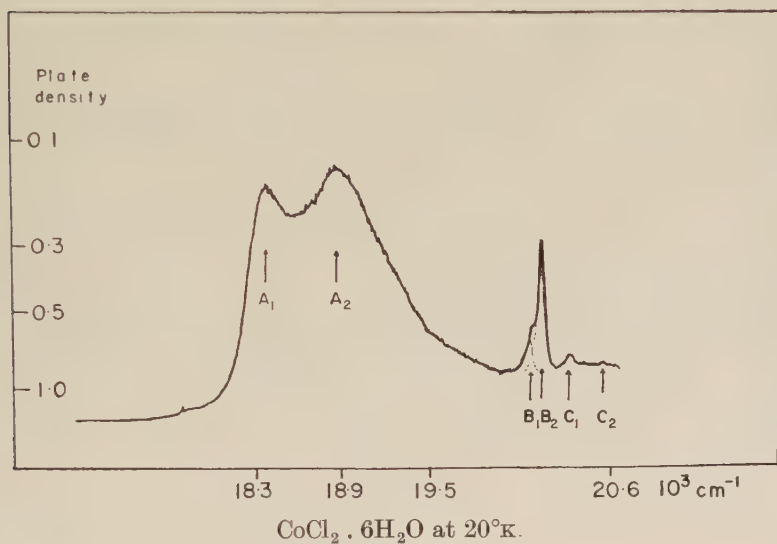


Fig. 6 (b)

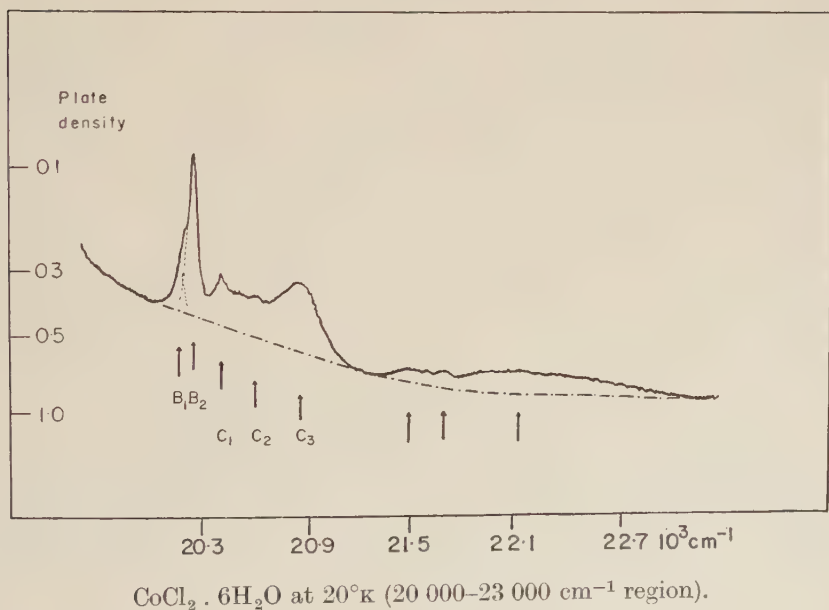
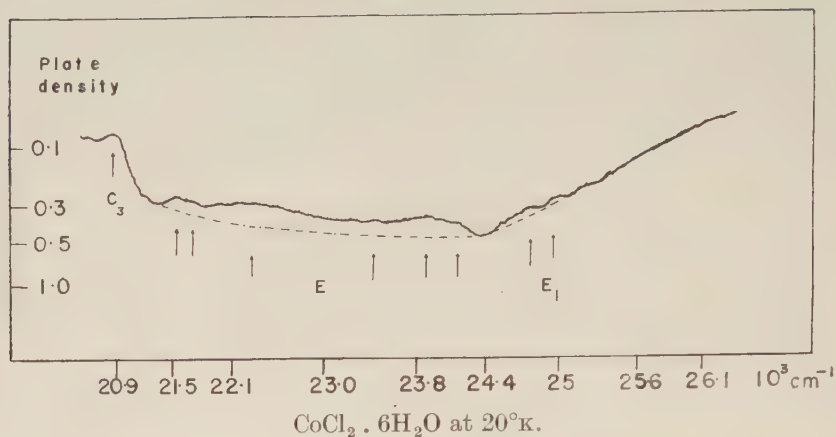


Fig. 6(c)

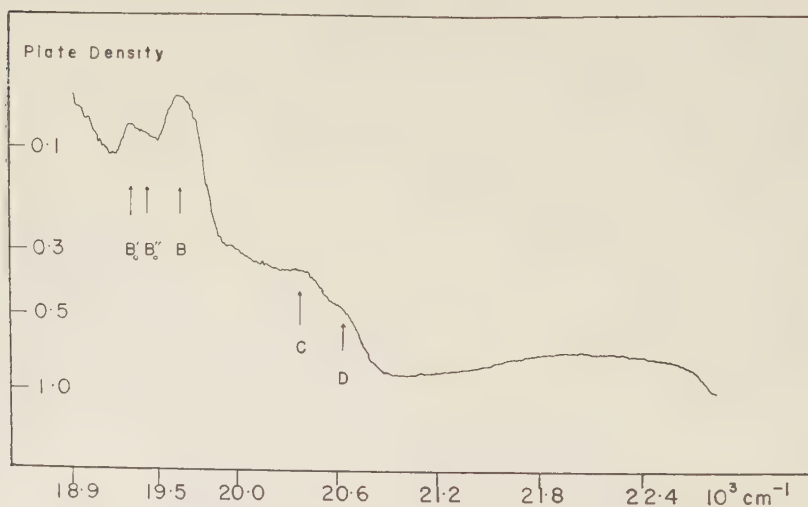


3.2. Cobalt Bromide

The spectrum is very similar to that of the chloride, apart for a general shift towards lower frequencies.

At room temperature the main absorption band in the yellow region has two not clearly resolved peaks at $18\,400$ and $18\,650\text{ cm}^{-1}$. As in the chloride, we have a weak doublet on the high-frequency side of the band at $\sim 19\,350$, with 105 cm^{-1} internal separation, followed by a stronger and broader line at $19\,700\text{ cm}^{-1}$.

Fig. 7



Detail of the absorption of $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ at room temperature.

On the high-frequency slope of the latter, shoulders appear at $20\,450$ and $20\,650$ (fig. 7) followed by a weak broad absorption from $21\,300$ to $23\,600$, with structure at $22\,200$ and $23\,000\text{ cm}^{-1}$.

At 90°K , as with the chloride, an increase in the resolution of the main band is observed. The peaks (fig. 8(a)), are now located at 18 130 and

Fig. 8(a)

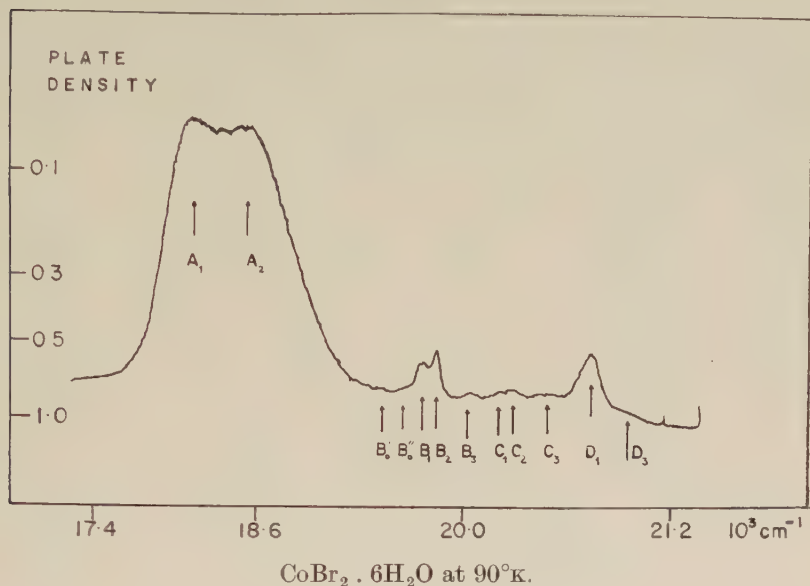
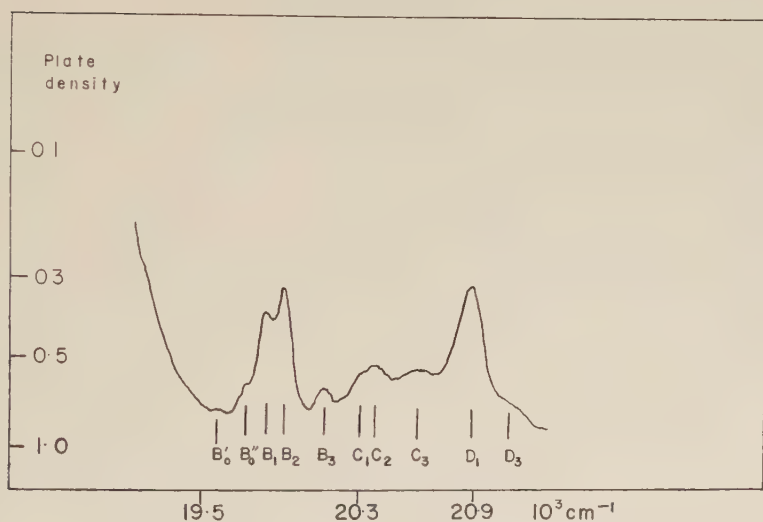


Fig. 8(b)

Detail of the absorption of $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ at 90°K .

$18\,550\text{ cm}^{-1}$. Towards the high-frequency side of this band, two diffuse lines are located at $19\,530$ and $19\,660\text{ cm}^{-1}$. After these there follows a doublet (B_1 and B_2) originating from the room temperature $19\,700\text{ cm}^{-1}$

absorption, with fairly equal components at $19\,770\text{ cm}^{-1}$ and $19\,860\text{ cm}^{-1}$ (fig. 8 (a), (b)).

Table 3. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ at 78°K

Absorpt. peaks and lines	Wave-number (cm^{-1})	Half-width (cm^{-1})	Relative intensity	Extinc. coeff. $\alpha_{\text{max}}(\text{cm}^{-1})$	Oscillator strength
$A_1^\dagger$	18420		0.95		
$A_2^\dagger$	18860		1		
B_0	19830 ‡				
B_1	20170	90	0.6	2.7	3.3×10^{-7}
B_2	20250	90	1	6	7.3×10^{-7}
C_1	20405				
C_2	(?)				
C_3	20815	300		4.2	1.7×10^{-6}
E	{ 21400 § 24400				
	24840	~ 60	1		
E_1	25030		1		
	25420		1		

† Peaks of main band (fig. 5 (a)).

‡ Sharp line.

§ Weak continuous absorption.

Then we observe a weak diffuse line (B_3) at $20\,075$, a partly resolved narrow absorption with shoulder (C_1) at $20\,260$ and peak at $20\,340\text{ cm}^{-1}$; another line of comparable intensity at $20\,560$ (C_3); finally an unresolved narrow band—of intensity and width similar to those of the B_1 , B_2 doublet—with peak (D_2) at $20\,840$ and a shoulder (D_3) at $21\,030\text{ cm}^{-1}$ (fig. 8 (b)).

Farther on towards higher frequencies a weak flat band with weak diffuse lines superposed stretches from $21\,400$ to $24\,440$.

At 20°K the new features are a sharp absorption (A_0) at $16\,500$, the changes in the B, C, D groups of lines and the appearance of line groups E, E_1 and F.

Nothing spectacular happens to the main band: the low frequency peak A_1 is moving slightly away from the other: in the bromide the first peak is stronger, just the opposite behaviour of the chloride (fig. 9 (a)).

In view of the changes they underwent, groups B, C, D have now the aspect of three triplets (fig. 9 (a)) with fairly constant internal separation and with a 500 cm^{-1} separation between the strongest line (B_2 , C_2 , D_2) of each triplet.

From densitometric readings the increase in the relative intensity of B_2 and C_2 is quite evident. A direct examination of the plates clearly shows that the maximum of the intensity in the $20\,800$ absorption is

shifting towards higher frequencies, so as to make the narrow band similar to the B_1B_2 and C_1C_2 doublets. On the whole, the close similarity of B, C, D line groups indicates a close relationship in these absorptions. The process of intensity decrease in B_1 and C_1 and corresponding increase in B_2 and C_2 suggests, as a most immediate explanation, a thermal redistribution of particles in two different closely lying ground states. We shall briefly return, in what follows, to this point.

Fig. 9(a)

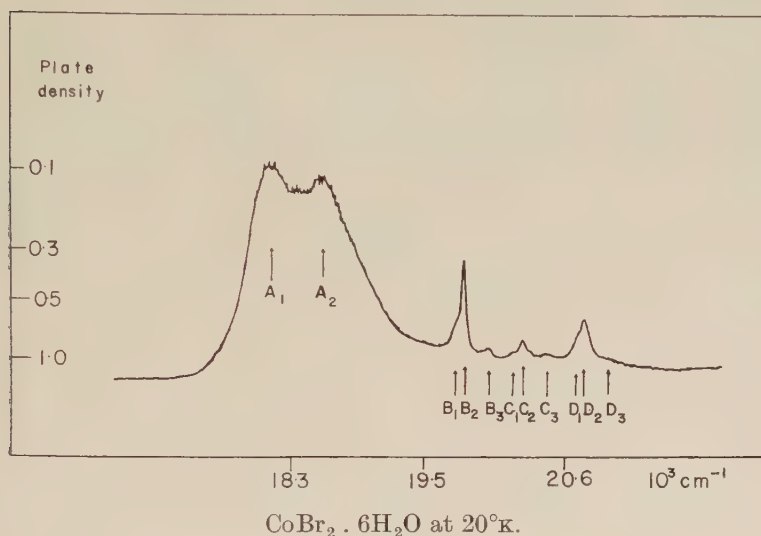
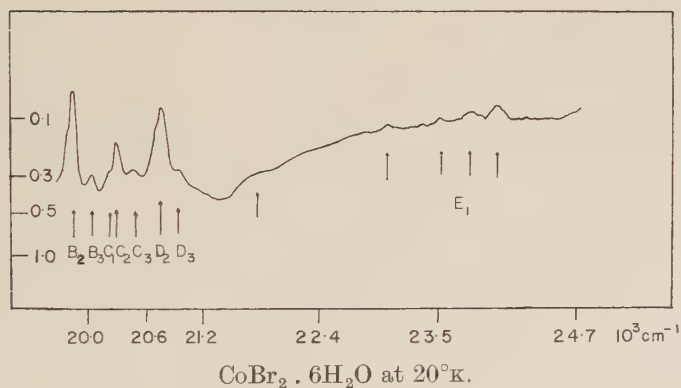


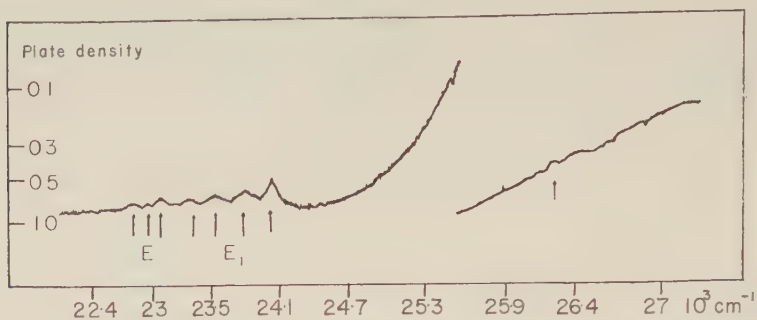
Fig. 9(b)



Line group E consists of a very sharp, weak doublet at 22950 and a stronger line at 23070; group E_1 includes a fairly strong broadish triplet (fig. 9(b)) at 23535, 23820, 24060 and also a very sharp weak line at 24375 cm^{-1} .

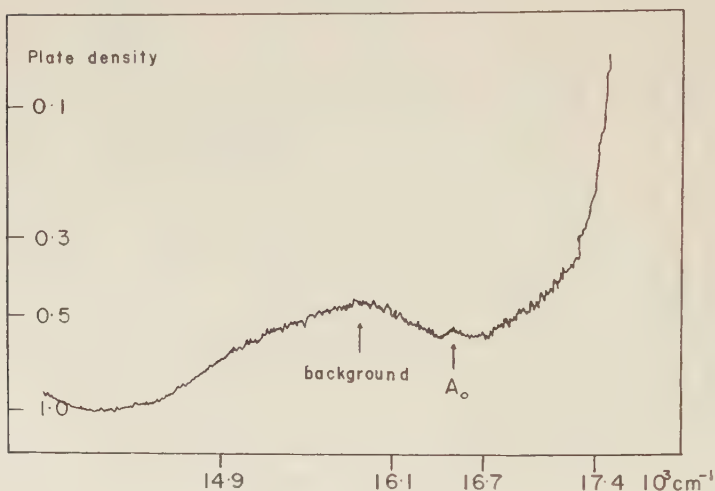
The F line at 26 250 seems to have a fine structure of three closely spaced components.

Fig. 9 (c)



Absorption lines of $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ at 20°K (22 500–27 000 cm^{-1} region).

Fig. 9 (d)



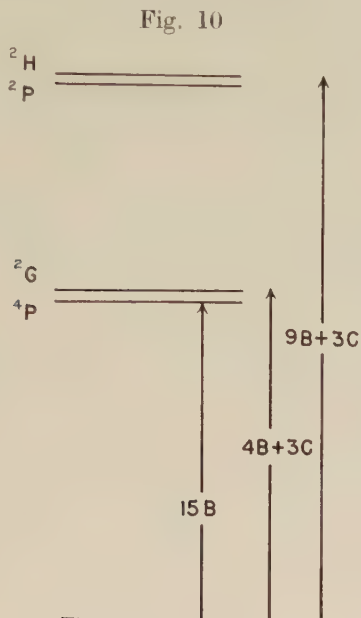
Detail of $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ at 20°K .

§ 4. ON THE INTERPRETATION OF EXPERIMENTAL RESULTS

We shall now compare the predictions of the ligand field theory with the experimental data.

For this purpose we start with the consideration of the Co^{2+} free ion. The set of levels for the $3d^7$ -system, in the case of the free ion, can be expressed in terms of Racah's parameter B and C (fig. 10), where for Co^{2+} , B has the value 971 cm^{-1} and $C \simeq 4, 6B$. The ^2H and ^2P levels are coincident only in first approximation. In a cubic field the maximum orbital degeneracy will be three, so that the free-ion orbital degeneracy will be partly lifted.

Using the 'strong field' formalism the following levels are obtained for Co^{2+} complex ion in a cubic field, omitting configuration interaction and spin-orbit coupling (Tanabe and Sugano 1954).



The excited levels of Co^{2+} (free ion). $B = 971 \text{ cm}^{-1}$, $C \simeq 4.6 B$.

Cubic field repres.	Subshell config.	Energy
$4F \left\{ \begin{array}{l} {}^4T_1 \\ {}^4T_2 \\ {}^4A_2 \end{array} \right.$	$d\epsilon^5 d\gamma^2$	$-8Dq - 12B$
	$d\epsilon^4 d\gamma^3$	$2Dq - 15B$
	$d\epsilon^3 d\gamma^4$	$12Dq - 15B$
$4P \left\{ \begin{array}{l} {}^4T_1 \end{array} \right.$	$d\epsilon^4 d\gamma^3$	$2Dq - 3B$
$2G \left\{ \begin{array}{l} {}^2A_1 \\ {}^2E \\ {}^a {}^2T_1 \\ {}^a {}^2T_2 \end{array} \right.$	$d\epsilon^4 d\gamma^3$	$2Dq - 11B + 3C$
	$d\epsilon^6 d\gamma$	$-18Dq - 8B + 4C$
	$d\epsilon^5 d\gamma^2$	$-8Dq - 6B + 3C$
	$d\epsilon^5 d\gamma^2$	$-8Dq - 2B + 3C$
$\begin{array}{l} {}^2H, {}^2P \\ {}^2D, {}^2F \end{array} \left\{ \begin{array}{l} {}^b {}^2T_1 \\ {}^b {}^2T_2 \\ {}^a {}^2T_1 \\ {}^b {}^2T_1 \\ {}^a {}^2T_2 \\ {}^b {}^2T_2 \\ \text{plus } {}^2E, {}^2T \text{ levels.} \end{array} \right.$	$d\epsilon^5 d\gamma^2$	$-8Dq - 2B + 3C$
	$d\epsilon^5 d\gamma^2$	$-8Dq + 6B + 5C$
	$d\epsilon^4 d\gamma^3$	$2Dq - 6B + 3C$
	$d\epsilon^4 d\gamma^3$	$2Dq + 3C$
	$d\epsilon^4 d\gamma^3$	$2Dq - 6B + 3C$
	$d\epsilon^4 d\gamma^3$	$2Dq + 4B + 3C$

In terms of group-theory, the eigenfunctions of levels with same multiplicity and same cubic field representation span the same subspace and so interact with each other. Namely, in the energy matrices pertaining to these levels there exists, besides the above-tabulated diagonal elements, non-diagonal elements, which are multiples of B and C (since we are in the strong-field formalism).

Table 4. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ at 20°K

Absorpt. peaks and lines	Wave-number (cm^{-1})	Half-width (cm^{-1})	Relative intensity	Extinc. coeff. $\alpha_{\text{max}}(\text{cm}^{-1})$	Oscillator strength
$A_0^\dagger$	17800				
$A_1^\ddagger$	18370		0.9		
$A_2^\ddagger$	18900		1		
B_1	20175§	~ 65	0.4	2.7	2.4×10^{-7}
B_2	20260	70	1	7	6.6×10^{-7}
C_1	20420	100		1.6	2.2×10^{-7}
C_2	20620				
C_3	20880	300		3.1	1.2×10^{-7}
E	21525			0.7	
	21710				
	21960				
	22150				
	23420				
	23590				
	23890				
E_1	24150			1.9	
	24785	~ 80			
E_1	25000				
	25440				
F	26300				

† Possible shoulder of main band.

‡ Main band peaks.

§ Extrapolated peak position; actual shoulder (fig. 6 (b)) at $20\,215\text{ cm}^{-1}$.

|| Structure of weak flat absorption (fig. 6 (b), (c)) from $21\,500$ to $24\,300\text{ cm}^{-1}$. Its total estimated oscillator strength $\sim 2 \times 10^{-6}$.

For the quartet $^4T_1$ levels the interaction energy is $6B$: taking into account this interaction the $^4T_1$ levels have energy

$$\frac{1}{2}[(-15B + 6Dq) \mp \sqrt{(225B^2 + 180Dq + 100Dq^2)}]. \quad (4.1)$$

Now the strongest transitions between the complex-ion levels are those leading from the ground state to states of the same multiplicity and involving, in general, only one electron jump in the $d\epsilon d\gamma$ subshells.

Thus we expect the transition:

$^4T_1 \rightarrow ^4T_2(^4F)$ to give rise to the infra-red band,

$^4T_1 \rightarrow ^4T_1(^4P)$ to give rise to the yellow band.

The corresponding observed energies in the $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ are respectively :

8.13 (sol.) 8.0 (cryst.) and 19.6 (sol.) 18.5 (cryst.)

in 10^3 cm^{-1} units, for the case of aqueous solutions and crystalline samples. It is possible, with the above assumptions, to work out the values of B_{sol} , Dq_{sol} and B_{cryst} , Dq_{cryst} , since the energy difference of the ${}^4T_1$ and ${}^4T_2$ levels is independent of C.

The values we thus obtain are the following :

$$B_{\text{sol}} = 860 \text{ cm}^{-1}, \quad Dq_{\text{sol}} = 950 \text{ cm}^{-1},$$

$$B_{\text{cryst}} = 775 \text{ cm}^{-1}, \quad Dq_{\text{cryst}} = 910 \text{ cm}^{-1}.$$

Table 5. $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ at Room Temperature

Absorpt. peaks and lines	Wave-number (cm^{-1})	Half-width (cm^{-1})	Relative intensity	Extinc. coeff. $\alpha_{\text{max}}(\text{cm}^{-1})$	Oscillator strength
$A_1^\dagger$	18400	2500		25	9×10^{-5}
$A_2^\dagger$	18650				
B_0'	19310				
B_0''	19420				
B	19700				
$C_+^\dagger$	20450			13	
$D_+^\dagger$	20650				
	22200§				
	22950§				
				1.7	

† Peaks of main band.

‡ See fig. 7.

§ Structure of 21 300–23 600 cm^{-1} band.

This means a considerable decrease of B not only from free ion to complex ion in solution, but also in the process of crystal formation. This is true also for Dq : both effects suggest that not only the ions of the first coordination sphere affect the 3d electronic orbitals, but a considerable influence is also due to second coordination ions.

In fact, as already mentioned, crystals of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ have a main absorption band in the visible at 20 000 cm^{-1} . A smaller difference is observed in the infra-red band of crystalline $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with peak at 8000 cm^{-1} and crystalline $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$ with peak at 8400 cm^{-1} .

Now it is known that the strength of ligand field increases in the order

$$\text{Br} < \text{Cl} < \text{F} < \text{O} < \text{N}$$

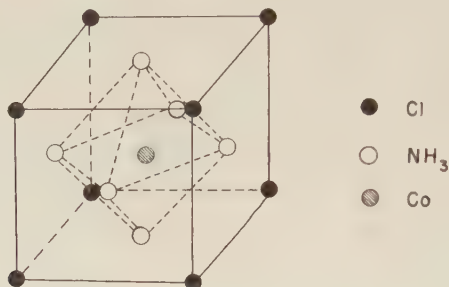
so that a substitution of anions, for instance Cl instead of Br, should determine a slight shift towards higher frequencies, as we actually observe. The same would happen if in turn Cl were to be substituted by fluorine

ions—in the fluosilicate—or oxygen ions—in aqueous solutions, where on the average the second coordination sphere will also contain water molecules.

4.1. *The Validity of a Cubic Field Approximation*

The preceding conclusions on B and Dq values are dependent on the validity of our assumption of a cubic field symmetry, namely supposing the six water molecules octahedrally arranged around the Co^{2+} ion.

Fig. 11



Disposition of anions and ligands in $\text{CoCl}_2 \cdot 6\text{NH}_3$.

Unfortunately there are no x-ray data for hydrated cobaltous chloride and bromide. For the corresponding ammoniate the x-ray investigation shows that actually $\text{CoCl}_2 \cdot 6\text{NH}_3$ has a structure of the cubic CaF_2 type, with lattice parameter $a = 9.87 \text{ \AA}$ and four molecules in the unit cell. The cobaltous ions are located at the corners and centres of the faces of a cube. Each Co^{2+} ion is in turn surrounded by six ammonia molecules arranged at the vertices of an octahedron intersecting the centres of the faces of a cube, whose corners are occupied by chlorine ions (fig. 11).

Now $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ is no longer cubic, as the corresponding ammoniate, but monoclinic with $a : b : c = 1.4788 : 1 : 0.9542$ and $\beta = 122^\circ 19'$. Yet, in terms of a local field, this may turn out to be only a distortion of the water molecule octahedron[†]; only x-ray study can settle the point.

However, if one assumes a predominant cubic field, any splitting of the levels due to non-cubic components ought to leave unchanged the centre of gravity of the intense absorption bands.

4.2. *The Position of Doublet Levels*

For the interpretation of spectra of crystals at low temperatures, the possibility of inter-system transitions has to be acknowledged. For this purpose we have to determine the position of the doublet levels pertaining to the $3d^7$ -system.

[†] Private communication from Professor M. H. L. Pryce (February 1958).

From the consideration of intra-system combination it was possible to deduce the values of B and Dq ; we need also the value of the C parameter for the evaluation of the doublet levels: from Tanabe and Sugano paper we assume $C \simeq 4.6B$.

There is first a couple of doublet levels not affected by configuration interaction

$${}^2A_1(d\epsilon^4 d\gamma^3),$$

$${}^2A_2(d\epsilon^4 d\gamma^3),$$

Using the obtained values of B and Dq , their distance from the ground state is respectively 21.7×10^3 and $37.1 \times 10^3 \text{ cm}^{-1}$.

On the other hand, the various ${}^2T_1$, ${}^2T_2$ and ${}^2E$ levels must be obtained by solving secular equations of fifth and fourth order, because neglect of configuration interaction remarkably affects the position of the levels.

In solving the secular equation for ${}^2T_1$ and ${}^2T_2$ (Tanabe and Sugano 1954) we have neglected for simplicity the $d\epsilon^3 d\gamma^4$ level in both cases, since they are widely separated from the four remaining states (the diagonal energy being respectively $12Dq + 5C$ and $12Dq - 6B + 3C$).

We solved numerically the corresponding secular equations assuming $B = 0.77$, $Dq = 0.91$ and $C = 4.6 B$ in 10^3 cm^{-1} units. The resulting separation from the ground level are:

Level	Subshell config.	No config. interact.	Config. interact.
${}_a {}^2T_2$	$d\epsilon^5 d\gamma^2$	$19.5 \times 10^3 \text{ cm}^{-1}$	$15.3 \times 10^3 \text{ cm}^{-1}$
${}_a {}^2T_2$	$d\epsilon^4 d\gamma^3$	25.6	23.4
${}_b {}^2T_2$	$d\epsilon^5 d\gamma^2$	32.8	33
${}_b {}^2T_2$	$d\epsilon^4 d\gamma^3$	33.3	39.1
${}^2T_2$	$d\epsilon^3 d\gamma^4$	46.4	

where the centre of gravity of the set of levels is roughly equal with or without configuration interaction. The configuration interaction is seen to influence strongly the position of the first and fourth level.

For the ${}^2T_1$ levels we have:

Levels	Subshell config.	No config. interact.	Config. interact.
${}_a {}^2T_1$	$d\epsilon^5 d\gamma^2$	$16.5 \times 10^3 \text{ cm}^{-1}$	$14.7 \times 10^3 \text{ cm}^{-1}$
${}_b {}^2T_1$	$d\epsilon^5 d\gamma^2$	19.6	19
${}_a {}^2T_1$	$d\epsilon^4 d\gamma^3$	25.6	24.7
${}_b {}^2T_1$	$d\epsilon^4 d\gamma^3$	30.2	33.3
${}^2T_1$	$d\epsilon^3 d\gamma^4$	35.1	

In the case of the ${}^2E$ doublets the secular equation is of the fourth order: we solved it numerically just as in the case of the ${}^2T_1$ and ${}^2T_2$

doublets. The obtained separation from the ground state is given by the following energy values.

Levels	Subshell config.	No config. interact.	Config. interact.
^2E	$d\epsilon^6 d\gamma$	$9.4 \times 10^3 \text{ cm}^{-1}$	$7.35 \times 10^3 \text{ cm}^{-1}$
^a_2E	$d\epsilon^4 d\gamma^3$	31	26.7
^2E	$d\epsilon^3 d\gamma^4$	34.7	32
^b_2E	$d\epsilon^4 d\gamma^3$	47	54.3

In fig. 12 are collected all the possible levels belonging to the $3d^7$ -system and obtained using the aforementioned set of parameters B, C and Dq.

Table 6. $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ at 90°K

Absorpt. peaks and lines	Wave- number (cm^{-1})	Half-width (cm^{-1})	Relative intensity	Extinc. coeff. $\alpha_{\text{max}}(\text{cm}^{-1})$	Oscillator strength
$A_1^\dagger$	18130		0.9		
	(18280?)				
$A_2^\dagger$	18550		1		
B_0'	19530				
B_0''	19660	75	0.5	1.4	1.5×10^{-7}
B_1	19770	95	0.8	3.3	4.5×10^{-7}
B_2	19860	100	1	4.5	6.5×10^{-7}
B_3	20075	75		1.3	1.4×10^{-7}
C_1	20260	} 200			
C_2	20340			2.3	6.6×10^{-7}
C_3	20560				
D_2	20840	250		4.5	1.6×10^{-6}
D_3	21030				
$E_1^\dagger$	23100				
$E_2^\dagger$	23830				
$E_3^\dagger$	24070			0.6	

† Peaks of main band.

‡ Broad lines superposed on weak flat absorption ranging from 21 400 to 24 440 cm^{-1} .

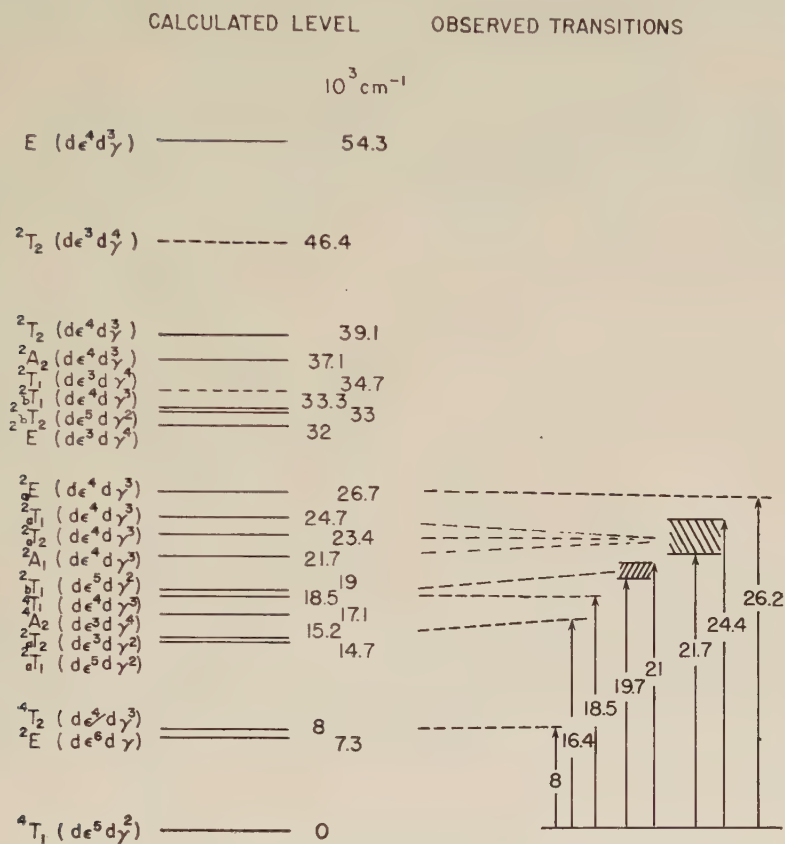
4.3. Comparison of Calculated Levels with Experimental Data

In the set of possible levels for cobalt halide hexahydrates tabulated in fig. 12 those characterized by greater transition probability are the upper quartet levels with subshell configuration $d\epsilon^4 d\gamma^3$, while quartet levels with occupation numbers $d\epsilon^3 d\gamma^4$ are expected to produce weaker and broader absorptions.

Transitions from the quartet ground state to doublet states are forbidden even in the presence of ligand field. They are made possible by doublet-quartet contamination, such as due, for example, by spin-orbit

coupling. Correspondingly, the intensity of such transitions will be smaller than that pertaining to intrasystem combinations.

Fig. 12



Calculated levels for $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (and $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$) and observed transitions.

As far as subshell configuration is concerned, the observation made for quartet-quartet transitions also applies to quartet-doublet transitions. The interesting point is that there are doublet levels with the same subshell configuration as the ground state, namely a^2T_1 , b^2T_1 , a^2T_2 , b^2T_2 ($d\epsilon^5 d\gamma^2$): their distance from the ground state is (neglecting configuration interaction) independent of Dq and thus of fluctuations of the strength of the ligand field. This case is most favourable for the presence in the absorption spectrum of sharp lines, even at relatively high temperatures (see for instance the case of Mn^{2+} , Gielesse 1935, Pappalardo 1957a).

At very low temperatures line structure may appear also in other transitions, involving variations in the occupation number of $d\epsilon$ and $d\gamma$,

as observed in the line structure of the main visible band of $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$ at 4°K (Pappalardo 1957 b).

Let us now consider, taking into account the aforementioned considerations, the spectrum of $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$, for instance; one observes that there is a remarkable good agreement with the theoretical predictions, if the following assignments are made:

Transition	Calc. value	Experiment
${}^4\text{T}_1 (\text{d}\epsilon^5 \text{d}\gamma^2) \rightarrow {}_a {}^2\text{T}_1, {}_a {}^2\text{T}_2 (\text{d}\epsilon^5 \text{d}\gamma^2)$	14700	16200 (?)
	15200	16450 (A_0)
$\rightarrow {}^4\text{T}_1 \quad (\text{d}\epsilon^4 \text{d}\gamma^3)$	18500	18500 (A)
$\rightarrow {}_a {}^2\text{T}_1 \quad (\text{d}\epsilon^5 \text{d}\gamma^2)$	19000	$\left\{ \begin{array}{l} 19745- \\ \quad \quad \quad (\text{B, C, D}) \\ 20980 \end{array} \right.$
$\rightarrow \left\{ \begin{array}{l} {}^2\text{A}_1 \quad (\text{d}\epsilon^4 \text{d}\gamma^3) \\ {}_a {}^2\text{T}_1, {}_a {}^2\text{T}_2 (\text{d}\epsilon^4 \text{d}\gamma^3) \end{array} \right.$	$\left\{ \begin{array}{l} 21700 \\ 23400-24700 \end{array} \right.$	$\left\{ \begin{array}{l} 21750- \\ \quad \quad \quad (\text{E, E}_1) \\ 24375 \end{array} \right.$
$\rightarrow {}_a {}^2\text{E} \quad (\text{d}\epsilon^4 \text{d}\gamma^3)$	26700	26250 (F)

The agreement is satisfactory not only for frequencies, but also in terms of the qualitative predictions made on the intensity of the various types of transitions, and on the temperature appearance of line structure. A better agreement for the energy levels could hardly be expected since spin-orbit coupling and non-cubic components of the field have been neglected.

4.4. The B, C, D Line Groups in the Bromide

A short discussion is required for these groups of lines in an attempt to explain the remarkable temperature effect observed in their intensity.

According to our tentative hypothesis these lines would be ascribed to the ${}^4\text{T}_1 \rightarrow {}^2\text{T}_1$ process. This assumption is supported by the weak frequency shift with temperature.

From ${}_a {}^2\text{T}_1$, taking into account all possible mechanisms lifting the spin degeneracy, a maximum of three levels can be obtained. This is true because the number of electrons is odd and thus the resulting levels are Kramers doublets.

Now if one assumes that the transition observed in these spectra are electric dipole transition, parity conservation requires, if the local symmetry of Co^{2+} has a centre of inversion, that the electronic transition be accompanied by emission (or absorption) of odd oscillations of the complex ion.

Koide and Pryce (1958) evaluate the frequency of such oscillations for $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ as 85, 170 and $320\text{--}400\text{ cm}^{-1}$. These frequency values explain nicely the internal triplet spacing observed in the B, C, D lines of the bromide, and also the disappearance at 20°K of the B_0' , B_0'' lines, if the latter are considered as representing an electronic transition and absorption from the lattice reservoir of an oscillation quantum.

Table 7. $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ at 20°K

Absorpt. peaks and lines	Wave-number (cm^{-1})	Half-width (cm^{-1})	Relative intensity	Extinc. coeff. (cm^{-1})	Oscillator strength
$\text{A}_0^\dagger$	16200(?)				
$\text{A}_1^\dagger$	16490				
$\text{A}_2^\dagger$	18120		0.9		
B_1	18600		1		
B_2	19745		0.5	3.1	
B_3	19830	60	1	7.5	6.5×10^{-7}
C_1	20040	75		2	2.2×10^{-7}
C_2	20245		0.7	1.3	
C_3	20325	100	1	2	3×10^{-7}
D_2	20515	125	0.7	1.3	2.4×10^{-7}
D_3	20805	140		4	8×10^{-7}
	20980			0.8	
	21750				
E	22770				
	22940§				
	23070	90	0.75	1.1	1.4×10^{-7}
	23250				
$\text{E}_{1 }$	23390(?)				
	23535		0.75		
	23820	140	0.9	1.8	3.6×10^{-7}
	24060	140	1	2.3	4.7×10^{-7}
F	24375 ⁽¹⁾				
	26250 ⁽²⁾				

† See fig. 9 (*d*).

‡ Peaks of main band.

§ Two lines 30 cm^{-1} apart.

|| Lines superposed on a weak flat band ranging from $21\ 400$ to $24\ 400\text{ cm}^{-1}$.

⁽¹⁾ Very weak, sharp.

⁽²⁾ Possibly consisting of three components.

The objection against this interpretation lies in the fact that the relative intensity of such doublets as B_1 , B_2 and C_1 , C_2 ought not to be altered from 90°K to 20°K , contrary to observation.

Another hypothesis has been previously advanced to explain this intensity *vs.* temperature effect in the B, C doublets of the bromide (and chloride), that is the existence of an upper ground state lying some 100 cm^{-1} over the fundamental state and interpreting the variation

in intensity as a process of thermodynamical distribution of the population in these two levels.

On the other hand, were this true, one would generally expect *all* the absorption lines to show a weak low-frequency satellite. This, from the examinations of the plates, seems very dubious, although it cannot decisively be ruled out owing to the weakness of the lines not belonging to the groups B, C and D.

§ 5. CONCLUSION

The agreement of the experimental data with the theory is certainly satisfactory. Many interesting properties of the spectra of these halides, such as the anion effect on the main band and the temperature effect on the intensity of some absorption lines deserve, undoubtedly, further investigations.

In this context it would be interesting to see if the cobalt chlorostannate is similar in its behaviour to the chloride or to the fluosilicate. A further study of these and the remaining halides extended to the ultra-violet and the near infra-red, using polarized light, will certainly be interesting to check some of the tentative hypothesis advanced.

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Intensity and Fine Structure of the Main Optical Absorption Bands in Hydrated Cobaltous Salts†

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ABSTRACT

The fine structure and the intensities of the main optical absorption bands in hydrated cobaltous salts are investigated theoretically on the basis of the crystal field theory. Calculations are made on the assumption that the crystal field is of cubic symmetry, and the same model as used in the previous calculation for Mn^{2+} salts is adopted for the normal vibrations of the complex. Reasonable agreements between observed and calculated results are obtained.

§ 1. INTRODUCTION

Of the various complexes of the first transition group elements with the configurations $3d^n$, $Co^{2+}(3d^7)$ ion is rather special in that the lowest level is a well-defined Kramers doublet even in a cubic field, due to the action of rather strong spin-orbit coupling and that the crystal field with lower symmetry is of minor importance. This situation considerably simplifies the theoretical analysis of the various properties of the cobaltous salts. For example the analysis of paramagnetic resonance data can be carried out by virtue of the spin-Hamiltonian with effective spin $\frac{1}{2}$. It may, therefore, be expected that the investigation of the behaviour of Co^{2+} ion will throw light on such a difficult problem as the detailed microscopic mechanism of the spin-lattice relaxation.

The paramagnetic resonance in hydrated cobaltous salts was investigated theoretically in great detail by Abragam and Pryce (1951). The temperature variation of the magnetic susceptibility was calculated by Kambe *et al.* (1952). These calculations are, however, mainly concerned with the lowest energy levels which come from the splitting of the lowest $^4T_{1g}$ state by the spin-orbit interaction. To clarify the nature of the higher states, it is necessary to analyse the data of the optical absorption experiments especially those obtained at low temperatures.

Energy matrices for the various states derived from $3d^7$ configuration have been given by Tanabe and Sugano (1954) in the case of cubic field apart from the fine structure due to the spin-orbit interaction, and, as far as the energy eigenvalues in this approximation are concerned, reasonable agreement has been obtained between experimental data and calculated positions of the absorption lines (Pappalardo 1959).

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As a further step in the quantitative investigation, we shall here calculate the fine-structure of the main optical absorption bands and estimate their intensities for $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$. As in the case of manganous salts (Koide and Pryce 1958, referred to as KP in the following), the calculation will be made in the strong field formalism. The same model as used there will also be adopted for the normal vibrations of the complex $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.

§ 2. WAVE FUNCTIONS

In this section we shall first set up the wave functions of the quartet states neglecting the effect of the spin-orbit interaction and the distorted component of the crystal field. As in KP, we shall denote the three $d\epsilon$ and the two $d\gamma$ functions by $\xi, \eta, \zeta; u, v$, whose angular parts are proportional to $yz/r^2, zx/r^2, xy/r^2, (3z^2 - r^2)/r^2$ and $(x^2 - y^2)/r^2$ respectively. By accommodating seven electrons in these orbits, we can get sixteen doublet and four quartet states. Since the ground Kramers doublet comes from a quartet state, we shall consider only the four quartet states in this paper. The explicit expressions of the wave functions for these quartets are as follows:

$${}^4T_{1g}: d\epsilon^4({}^3T_{1g})d\gamma^3({}^2E_g). \quad \left. \begin{aligned} |\alpha_1'\rangle &= -\frac{1}{2} [\xi\bar{\xi}\eta\zeta uv\bar{v}] + \frac{\sqrt{3}}{2} [\xi\bar{\xi}\eta\zeta u\bar{u}v], \\ |\beta_1'\rangle &= +\frac{1}{2} [\xi\eta\bar{\eta}\zeta uv\bar{v}] + \frac{\sqrt{3}}{2} [\xi\eta\bar{\eta}\zeta u\bar{u}v], \\ |\gamma_1'\rangle &= [\xi\eta\zeta\bar{\zeta} uv\bar{v}]. \end{aligned} \right\} \quad \cdot \cdot \cdot \quad (1a)$$

$${}^4T_{1g}: d\epsilon^5({}^2T_{2g})d\gamma^2({}^3A_{2g}). \quad \left. \begin{aligned} |\alpha_2'\rangle &= [\xi\eta\bar{\eta}\zeta\bar{\zeta} uv], \\ |\beta_2'\rangle &= [\xi\bar{\xi}\eta\zeta\bar{\zeta} uv], \\ |\gamma_2'\rangle &= [\xi\bar{\xi}\eta\bar{\eta}\zeta uv]. \end{aligned} \right\} \quad \cdot \cdot \cdot \quad (1b)$$

$${}^4A_{2g}: d\epsilon^3({}^4A_{2g})d\gamma^4({}^1A_{1g}). \quad |{}^4A_{2g}\rangle = [\xi\eta\zeta u\bar{u}v\bar{v}]. \quad \cdot \cdot \cdot \quad (1c)$$

$${}^4T_{2g}: d\epsilon^4({}^3T_{1g})d\gamma^3({}^2E_g). \quad \left. \begin{aligned} |\alpha_3\rangle &= \frac{\sqrt{3}}{2} [\xi\bar{\xi}\eta\zeta uv\bar{v}] + \frac{1}{2} [\xi\bar{\xi}\eta\zeta u\bar{u}v], \\ |\beta_3\rangle &= \frac{\sqrt{3}}{2} [\xi\eta\bar{\eta}\zeta uv\bar{v}] - \frac{1}{2} [\xi\eta\bar{\eta}\zeta u\bar{u}v], \\ |\gamma_3\rangle &= -[\xi\eta\zeta\bar{\zeta} u\bar{u}v]. \end{aligned} \right\} \quad \cdot \cdot \cdot \quad (1d)$$

Here the bracket notation stands for the normalized Slater determinant and the orbitals without bar include up-spin and with bar down-spin functions respectively. For brevity, here we have written down the states with maximum M_s value ($=\frac{3}{2}$) and omitted the closed shell configuration common to all. Two sets of ${}^4T_{1g}$ states are coupled with each other and the

energy matrix for these states is given by

$$\begin{bmatrix} \frac{2}{10} \Delta - 3B & -6B \\ -6B & -\frac{8}{10} \Delta - 12B \end{bmatrix} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where Δ is the energy difference between $d\gamma$ and $d\epsilon$ orbitals and $B = F_2 - 5F_4$ is a parameter introduced by Racah (Tanabe and Sugano 1954). By diagonalizing this matrix, we can get the eigenfunctions and eigenvalues of the two ${}^4T_{1g}$ states as follows:

$$|\alpha_1\rangle = \cos \theta |\alpha_1'\rangle - \sin \theta |\alpha_2'\rangle \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

$$|\alpha_2\rangle = \sin \theta |\alpha_1'\rangle + \cos \theta |\alpha_2'\rangle \quad . \quad . \quad . \quad . \quad . \quad (3b)$$

Similar expressions for β_1 , β_2 and γ_1 , γ_2 , and

$$\left. \begin{aligned} E_1 &= \frac{1}{2} \{ -\frac{3}{5} \Delta - 15B + (\Delta^2 + 18\Delta B + 225B^2)^{1/2} \}, \\ E_2 &= \frac{1}{2} \{ -\frac{3}{5} \Delta - 15B - (\Delta^2 + 18\Delta B + 225B^2)^{1/2} \}, \end{aligned} \right\} \quad . \quad . \quad . \quad (4)$$

where θ is given by

$$\tan 2\theta = 12B/(\Delta + 9B) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The energy values of the ${}^4A_{2g}$ and ${}^4T_{2g}$ states are

$$E_4 = \frac{12}{10} \Delta - 15B \quad \text{and} \quad E_3 = \frac{2}{10} \Delta - 15B$$

respectively.

For $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ crystal, Pappalardo (1959) determined values of the parameters Δ and B as

$$\Delta = 9100 \text{ cm}^{-1} \quad \text{and} \quad B = 775 \text{ cm}^{-1} \quad . \quad . \quad . \quad . \quad (6)$$

so as to get good agreement between calculated and observed positions of the spectral lines.

§ 3. SPIN-ORBIT INTERACTION

We now introduce the spin-orbit interaction $H_{so} = \zeta_d \sum \mathbf{l}_j \cdot \mathbf{s}_j$ as a small perturbation and investigate the fine-structure splittings of the ${}^4T_{1g}$ levels. By straightforward calculation (or by the use of Tanabe and Kamimura's recently published tables (1958)), we can easily obtain the matrix elements of H_{so} . Using eqns. (3) and the relationship

$$\begin{aligned} -2\langle \mu_1'(M_s) | H_{so} | \nu_1'(M_s') \rangle &= \langle \mu_1'(M_s) | H_{so} | \nu_2'(M_s') \rangle \\ &= \langle \mu_2'(M_s) | H_{so} | \nu_2'(M_s') \rangle = \langle \mu_2'(M_s) | H_{so} | \nu_1'(M_s') \rangle \quad . \quad . \quad (7) \\ &\quad (\text{for } \mu, \nu = \alpha, \beta, \gamma) \end{aligned}$$

we can get

$$\langle \mu_n(M_s) | H_{so} | \nu_n(M_s') \rangle = C_n \langle \mu_1(M_s) | H_{so} | \nu_1(M_s') \rangle \quad . \quad . \quad . \quad (8)$$

where

$$\left. \begin{aligned} C_1 &= \cos^2 \theta - 2 \sin^2 \theta + 2 \sin 2\theta, \\ C_2 &= \sin^2 \theta - 2 \cos^2 \theta - 2 \sin 2\theta. \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (9)$$

To express the matrix of H_{so} , it is more convenient to use

$$\left. \begin{aligned} |\chi_n^+(M_s)\rangle &= -\frac{1}{\sqrt{2}}\{|\alpha_n(M_s)\rangle + i|\beta_n(M_s)\rangle\}, \\ |\chi_n^-(M_s)\rangle &= \frac{1}{\sqrt{2}}\{|\alpha_n(M_s)\rangle - i|\beta_n(M_s)\rangle\}, \end{aligned} \right\} \quad \dots \quad (10)$$

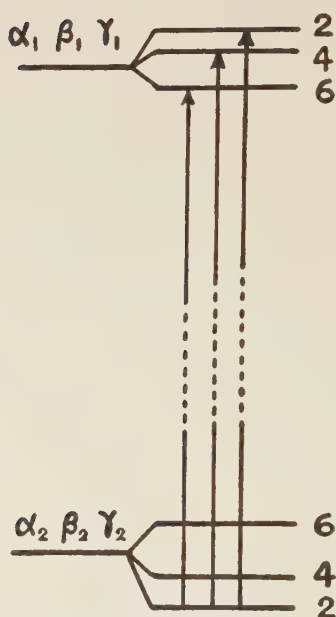
instead of $|\alpha_n\rangle$ and $|\beta_n\rangle$. Then the matrix breaks up into

$$\begin{array}{l} \chi_n^{\mp}(\pm \frac{3}{2}) \\ \chi_n^{\pm}(\mp \frac{1}{2}) \\ \gamma_n(\pm \frac{1}{2}) \end{array} \left[\begin{array}{ccc} \chi_n^{\mp}(\pm \frac{3}{2}) & \chi_n^{\pm}(\mp \frac{1}{2}) & \gamma_n(\pm \frac{1}{2}), \\ \frac{1}{4}C_n \zeta_d & 0 & \frac{1}{2\sqrt{6}}C_n \zeta_d \\ 0 & \frac{1}{12}C_n \zeta_d & \frac{1}{3\sqrt{2}}C_n \zeta_d \\ \frac{1}{2\sqrt{6}}C_n \zeta_d & \frac{1}{3\sqrt{2}}C_n \zeta_d & 0 \end{array} \right] \quad (11)$$

$$\begin{array}{l} \chi_n^{\pm}(\pm \frac{1}{2}) \\ \gamma_n(\pm \frac{3}{2}) \end{array} \left[\begin{array}{cc} \chi_n^{\pm}(\pm \frac{1}{2}) & \gamma_n(\pm \frac{3}{2}) \\ -\frac{1}{12}C_n \zeta_d & \frac{1}{2\sqrt{6}}C_n \zeta_d \\ \frac{1}{2\sqrt{6}}C_n \zeta_d & 0 \end{array} \right] \quad \dots \quad (12)$$

$$\chi_n^{\pm}(\pm \frac{3}{2}): -\frac{1}{4}C_n \zeta_d. \quad \dots \quad (13)$$

Fig. 1



Fine structure splittings of the ${}^4T_{1g}$ levels.
(The numbers shown are the degeneracies of the levels.)

If we neglect the off-diagonal elements of H_{so} between $(\chi_1^+, \chi_1^-, \gamma_1)$ and $(\chi_2^+, \chi_2^-, \gamma_2)$, and assume the perfectly cubic crystal field, the eigenfunctions can be obtained by diagonalizing each of these matrices as:

$$\sqrt{\frac{1}{2}}|\chi_n^{\mp}(\pm\frac{3}{2})\rangle + \sqrt{\frac{1}{6}}|\chi_n^{\pm}(\mp\frac{1}{2})\rangle + \sqrt{\frac{1}{3}}|\gamma_n(\pm\frac{1}{2})\rangle, \quad (14a)$$

$$\left. \begin{aligned} & -\sqrt{\frac{2}{5}}|\chi_n^{\mp}(\pm\frac{3}{2})\rangle + \sqrt{\frac{8}{15}}|\chi_n^{\pm}(\mp\frac{1}{2})\rangle + \sqrt{\frac{1}{15}}|\gamma_n(\pm\frac{1}{2})\rangle \\ & \sqrt{\frac{2}{5}}|\chi_n^{\pm}(\pm\frac{1}{2})\rangle + \sqrt{\frac{3}{5}}|\gamma_n(\pm\frac{3}{2})\rangle \end{aligned} \right\} \quad (14b)$$

$$\left. \begin{aligned} & -\sqrt{\frac{1}{10}}|\chi_n^{\mp}(\pm\frac{3}{2})\rangle - \sqrt{\frac{3}{10}}|\chi_n^{\pm}(\mp\frac{1}{2})\rangle + \sqrt{\frac{3}{5}}|\gamma_n(\pm\frac{1}{2})\rangle \\ & \sqrt{\frac{3}{5}}|\chi_n^{\pm}(\pm\frac{1}{2})\rangle - \sqrt{\frac{2}{5}}|\gamma_n(\pm\frac{3}{2})\rangle \end{aligned} \right\} \quad (14c)$$

The eigenvalues of the spin-orbit interaction energy for these states are

$$\frac{5}{12}C_n\zeta_d \text{ for (14a) (doublet)}$$

$$\frac{1}{6}C_n\zeta_d \text{ for (14b) (quartet)}$$

$$-\frac{1}{4}C_n\zeta_d \text{ for (14c) (sextet)}$$

respectively. For the value of θ obtained from (5) and (6),

$$C_1 = 1.80 \quad \text{and} \quad C_2 = -2.80. \quad (15)$$

The spin-orbit interaction parameter λ of the expression $H_{so} = \lambda \mathbf{L} \cdot \mathbf{S}$ is -180 cm^{-1} for ^4F state of the free Co^{2+} ion. Since $\zeta_d = -3\lambda$ for ^4F states

$$\zeta_d = 540 \text{ cm}^{-1}, \quad (16)$$

yielding $C_1\zeta_d = 970 \text{ cm}^{-1}$ and $C_2\zeta_d = -1510 \text{ cm}^{-1}$. Thus we know each of the two $^4T_{1g}$ levels splits into three levels, and, as C_2 is negative, the ground level is a well-defined Kramers doublet given by (14a) for $n=2$. Since the second lowest level lies at about

$$\frac{1}{4}C_2\zeta_d = 380 \text{ cm}^{-1} \simeq (500^\circ\text{K}) \times k$$

above the ground level, the transitions are mostly expected from the ground level. These levels are shown in fig. 1.

§ 4. INTENSITY CALCULATION

Since all states derived from $3d^7$ configuration are of even parity, a small amount of mixing of odd electronic states must be taken into consideration to account for the electric dipole transitions. Such mixing takes place through the interaction with the odd vibrations of the complex ion. We treat the complex ion $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ as an isolated unit and adopt the same point-dipole model as in KP, and denote the normal coordinates of the modes T_{1u} (frequency ν_3), $T_{1u}(\nu_4)$ and $T_{2u}(\nu_6)$ as (Q_{3x}, Q_{3y}, Q_{3z}) , (Q_{4x}, Q_{4y}, Q_{4z}) and (Q_{6x}, Q_{6y}, Q_{6z}) respectively. Although the mass of the central ion (Co^{2+}) is slightly different from that of Mn^{2+} , the same normal coordinates will be used in the present calculation since in any case we have been forced to use approximations in other respects. Then (see fig. 2)

$$Q_{3x} = \sqrt{(4/5)}X_0 + \sqrt{(4/45)}(X_1 + X_2) - \sqrt{(5/36)}(X_3 + X_4 + X_5 + X_6), \quad (17a)$$

$$Q_{4x} = \sqrt{(6/5)}X_0 - \sqrt{(3/10)}(X_1 + X_2), \quad (17b)$$

$$Q_{6x} = (X_3 + X_4 - X_5 - X_6)/2, \quad (17c)$$

and $h\nu_3 = 85 \text{ cm}^{-1}$, $h\nu_4 = 320 \text{ cm}^{-1}$ and $h\nu_6 = 170 \text{ cm}^{-1}$. (18)

This value of ν_4 has been determined by the use of the approximate relation $\nu_4 = (5/3)^{1/2} \nu_1$ and of the value $\nu_1 \simeq \nu_2 \simeq 250 \text{ cm}^{-1}/h$ obtained by Schultz (1942) (cf. KP § 6).

The perturbation responsible for the mixing of odd states is

$$H_v = \sum_i (\partial V / \partial Q_i)_{Q=0} Q_i,$$

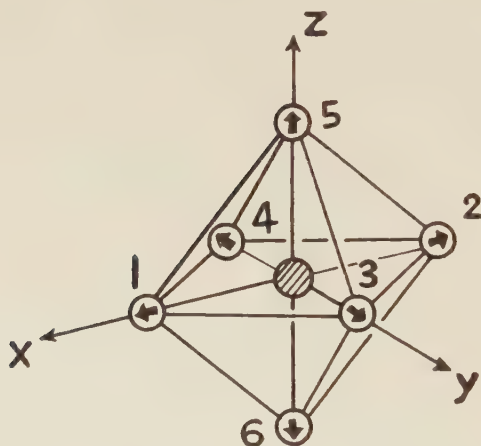
where $V = \sum_s v(x_s, y_s, z_s; Q)$ is the potential due to the crystal field and x_s, y_s, z_s are the coordinates of sth electron. In the following $(\partial v / \partial Q_{jx})_{Q=0}$ etc. will be denoted by u_{jx} etc., then

$$H_v = \sum_{s=1}^7 \sum_{j=3,4,6} \sum_{w=x,y,z} u_{jw}(x_s, y_s, z_s) Q_{jw}. \quad (19)$$

The matrix element of the dipole moment vector P between initial and final states through intermediate states with odd parity is given by:

$$\begin{aligned} \langle {}^4i : n | P | {}^4f : n' \rangle &= \sum_k \frac{\langle {}^4i : n | H_v | {}^4k : n' \rangle \langle {}^4k : n' | P | {}^4f : n' \rangle}{E_i - E_k} \\ &+ \sum_k \frac{\langle {}^4i : n | P | {}^4k : n \rangle \langle {}^4k : n | H_v | {}^4f : n' \rangle}{E_f - E_k}, \quad (20) \end{aligned}$$

Fig. 2



The model of the octahedral complex.

where each of n and n' stands for a set of the vibrational quantum numbers. Since the main contribution will come from such intermediate states in which one of the seven $3d$ electrons is promoted to a $4p$ orbit, it will be a good approximation to replace $E_k - E_i \simeq E_k - E_f$ by an appropriate mean value of the energy difference ΔE between $3d^6 4p$ and $3d^7$ configurations of a Co^{2+} ion. Then, using the closure properties of the eigenfunctions, we can reduce (20) to

$$\langle {}^4i : n | P | {}^4f : n' \rangle = \langle {}^4i : n | P H_v | {}^4f : n' \rangle (-2/\Delta E).$$

Furthermore, this can be factorized as

$$= (-2/\Delta E) \sum_{j,w} \langle n | Q_{jw} | n' \rangle \langle {}^4i | \sum_s p(\mathbf{r}_s) u_{jw}(\mathbf{r}_s) | {}^4f \rangle.$$

Since at low temperatures no molecular vibration is excited in the initial states, the final vibrational state is one of such states in which only one vibrational quantum is excited. Then

$$\langle {}^4i : 0 | P | {}^4f : n_{jw} = 1 \rangle = (-2/\Delta E) (h/2M\omega_j)^{1/2} \langle {}^4i | \sum_s p(\mathbf{r}_s) u_{jw}(\mathbf{r}_s) | {}^4f \rangle, \quad (21)$$

where M is the mass of a ligand. The non-vanishing matrix elements of the electronic part are listed in table 1.

Table 1. Non-vanishing Matrix Elements of the Electronic Part of eqn. (21): $\langle {}^4i | \sum_s p(\mathbf{r}_s) u_{jw}(\mathbf{r}_s) | {}^4f \rangle$

Initial state (i)	Final state (f)	Direction of the vibration (w)	Direction of the dipole moment vector	Matrix element
α_2 β_2 γ_2	α_1 β_1 γ_1	x y z	x y z	$\frac{1}{2} \sin 2\theta (I_{j1} + I_{j2} - 2I_{j3})$
α_2 β_2 γ_2	α_1 β_1 γ_1	y, z z/x x, y	y, z z/x x, y	$\frac{1}{2} \sin 2\theta (I_{j4} - I_{j2})$
α_2 α_2 β_2 β_2 γ_2 γ_2	β_1 γ_1 γ_1 α_1 α_1 β_1	x x y y z z	y z z x x y	$\frac{1}{4} I_{j5} \sin 2\theta + \frac{1}{2} I_{j6}$ $-\frac{\sqrt{3}}{2} I_{j7} \cos 2\theta$
α_2 α_2 β_2 β_2 γ_2 γ_2	β_1 γ_1 γ_1 α_1 α_1 β_1	y z z x x y	x x y y z z	$\frac{1}{4} I_{j5} \sin 2\theta - \frac{1}{2} I_{j6}$ $-\frac{\sqrt{3}}{2} I_{j7} \cos 2\theta$

$$I_{i1} = (v | u_{jz} \cdot z | v), \quad I_{j2} = (\zeta | u_{jz} \cdot z | \zeta), \quad I_{j3} = (\xi | u_{jz} \cdot z | \xi), \quad I_{j4} = (v | u_{jx} \cdot x | v), \\ I_{i5} = (\xi | u_{jx} \cdot y | \eta), \quad I_{j6} = (\zeta | u_{jx} \cdot y | v), \quad I_{j7} = (\zeta | u_{jx} \cdot y | u).$$

As in KP we shall assume that the crystal field is due to the six point dipoles of moment μ vibrating about the equilibrium positions $(\pm R, 0, 0)$, $(0, \pm R, 0)$ and $(0, 0, \pm R)$ without changing their directions given by $(\pm 1, 0, 0)$, $(0, \pm 1, 0)$ and $(0, 0, \pm 1)$ respectively. Then u_{3z} , u_{4z} and u_{6z} are

given by

$$\left. \begin{aligned} u_{3z} &= \frac{18}{\sqrt{5}} \mathcal{Y}_{10} - \frac{45}{\sqrt{5}} \mathcal{Y}_{30} + \frac{315}{4\sqrt{5}} \mathcal{Y}_{50} + \frac{63\sqrt{7}}{4} \mathcal{Y}_{54}, \\ u_{4z} &= -\frac{36}{\sqrt{30}} \mathcal{Y}_{10} - \frac{260}{\sqrt{30}} \mathcal{Y}_{30} - \frac{315}{\sqrt{30}} \mathcal{Y}_{50} + \frac{147}{\sqrt{42}} \mathcal{Y}_{54}, \\ u_{6z} &= 5\sqrt{15} \mathcal{Y}_{32} - \frac{7\sqrt{105}}{2} \mathcal{Y}_{52}, \end{aligned} \right\} \quad (22)$$

where

$$\left. \begin{aligned} \mathcal{Y}_{10} &= \left(\frac{4\pi}{2l+1} \right)^{1/2} \frac{e\mu r^l}{R^{l+3}} Y_l^0, \\ \mathcal{Y}_{lm} &= \left(\frac{4\pi}{2l+1} \right)^{1/2} \frac{e\mu r^l}{R^{l+3}} \frac{Y_l^m + Y_l^{-m}}{\sqrt{2}} \end{aligned} \right\} \quad \dots \dots \dots (28)$$

for $l=1, 3, 5$ and $m=2, 4$ †.

Table 2. Calculated Oscillator Strengths of the Transitions to the Upper ${}^4T_{1g}$ States

Electronic levels	Relevant vibrations		
	T_{1u} $h\nu_3=170 \text{ cm}^{-1}$	T_{1u} $h\nu_4=320 \text{ cm}^{-1}$	T_{2u} $h\nu_6=85 \text{ cm}^{-1}$
Doublet	0.3×10^{-5}	0.6×10^{-5}	0.4×10^{-5}
Quartet	1.5	0.8	1.1
Sextet	7.6	1.8	3.0
Total	1.7×10^{-4}		

Experimental values of the total oscillator strength is about 10^{-4} at room temperature (Pappalardo 1958).

The numerical values of the matrix elements depend on the quantities

$$\frac{e\mu}{R^2} \langle \frac{r^2}{R^2} \rangle, \quad \frac{e\mu}{R^2} \langle \frac{r^4}{R^4} \rangle \quad \text{and} \quad \frac{e\mu}{R^2} \langle \frac{r^6}{R^6} \rangle, \quad \dots \dots \dots (24)$$

where $\langle \rangle$ represents the average with respect to the radial part of the $3d$ functions. Since the non-empirical calculation of $\langle r^n \rangle$ is extremely difficult and the values of μ and R are not known, it is almost impossible to evaluate these quantities theoretically. If, however, we assume that the crystal field splitting Δ is entirely due to the electrostatic field created by the six point dipoles mentioned above, there is the relationship

$$\Delta = \frac{25}{3} \frac{e\mu}{R^2} \langle \frac{r^4}{R^4} \rangle. \quad \dots \dots \dots (25)$$

† As to the expressions for the x -components u_{jx} , see (4.16) and (4.17) in KP. The relations between u_{jx} and v_{ix} in KP are

$$u_{3x} = 6v_{1x}/\sqrt{5}, \quad u_{4x} = (8v_{1x} + 10v_{2x})/\sqrt{30} \quad \text{and} \quad u_{6x} = v_{3x}.$$

This and (6) give

$$\frac{e\mu}{R^2} \left\langle \frac{r^4}{R^4} \right\rangle = 1092 \text{ cm}^{-1}. \quad (26)$$

As to the other two, we tentatively assume the following values of the ratios (cf. KP);

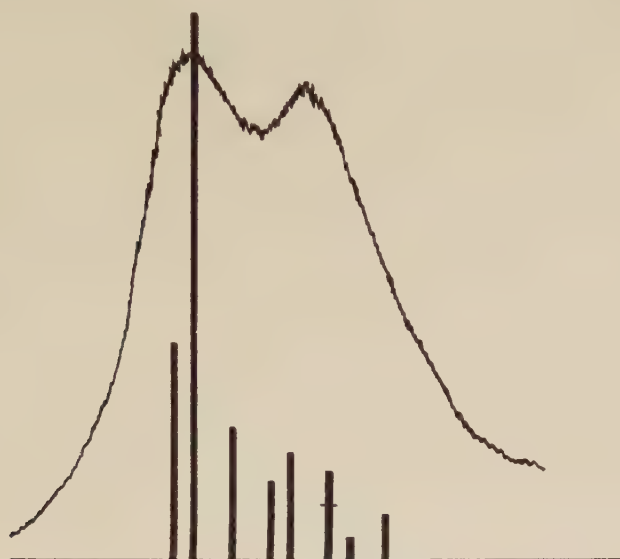
$$\frac{\langle r^2/R^2 \rangle}{\langle r^4/R^4 \rangle} = 4 \quad \text{and} \quad \frac{\langle r^6/R^6 \rangle}{\langle r^4/R^4 \rangle} = 0.3. \quad (27)$$

Table 2 shows the numerical results for the transitions to the upper ${}^4T_{1g}$ states obtained by making use of the values (6), (18), (26), (27) and

$$\Delta E = 10^5 \text{ cm}^{-1} \quad (28)$$

obtained from the spectral data of the free Co^{2+} ion (Moore 1952). Figure 3 shows how the calculated results compare with Pappalardo's observations.

Fig. 3



Comparison of the calculated intensities of the transitions to the ${}^4T_{1g}$ states with experimental absorption spectrum of $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ obtained by Pappalardo (1958) at 20°K .

The total intensities (oscillator strengths) of the transitions to ${}^4A_{2g}$ and ${}^4T_{2g}$ states calculated in the same way are

$${}^4T_{1g} \rightarrow {}^4A_{2g} : f = 4.8 \times 10^{-6}$$

$${}^4T_{1g} \rightarrow {}^4T_{2g} : f = 4.0 \times 10^{-5}.$$

The observed value for the latter (infra-red; $h\nu \simeq 8000 \text{ cm}^{-1}$) is 3×10^{-5} for $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (Holmes and McClure 1957). The ${}^4A_{2g}$ states have the configuration $d\epsilon^3 d\gamma^4$ and have matrix elements of PH_v only with the minor mixed components $|\alpha_1'\rangle$, $|\beta_1'\rangle$ and $|\gamma_1'\rangle$ in the ground states. (Roughly speaking, the transition to ${}^4A_{2g}$ is a double jump, i.e. $d\epsilon^5 d\gamma^2 \rightarrow d\epsilon^3 d\gamma^4$.)

The intensity is, therefore, proportional to $\sin^2 \theta$ and is very small. Since the lines corresponding to this transition are expected very near to the main visible bands, the peaks would be masked by the latter.

§ 5. CONCLUSION

Since the transitions from the ground ${}^4T_{1g}$ to the upper ${}^4T_{1g}$ (main visible band) can be regarded approximately as the jump of a $d\epsilon$ electron to a $d\gamma$ orbit, it gives rise to an appreciable change of the charge cloud, and, as the result, causes the excitation of even vibrations. The observed absorption corresponding to each of the calculated lines are, therefore, expected to be a broad band with tail mainly in the high frequency side of the original line. When we compare the observed spectrum with the calculated one, we must bear this fact in mind.

In our calculation, many unknown quantities are involved, e.g. frequencies of the odd vibrations, values of (24), (28) etc. Furthermore, there might be some distortion of the crystal field from the cubic symmetry, which adds still more parameters. It is, however, hopeless at the present stage to regard these as adjustable parameters and to determine their values so as to get good agreement with experimental data. We have, therefore, used the tentative values (18), (26) and (27), and neglected the effect of the distorted field. In spite of these ambiguities, the general results are in good agreement with experiment. To go far in detail, one must refer to some more experimental information, e.g. crystal structure, paramagnetic resonance data etc.

ACKNOWLEDGMENTS

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Adhesion of Evaporated Aluminium Films with Underlayers of Nickel, Cobalt and Chromel†

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[Received November 10, 1958]

ABSTRACT

Thin layers of nickel, cobalt and chromel are evaporated under vacuum on to glass microscope slides and used as underlayers for aluminium films. Adhesion measurements are used to investigate ageing effects which are shown to depend upon temperature as well as the nature and thickness of the underlayer. Results are shown to be due to intermetallic compound formation at the interface causing a type of age-hardening which may result in either decrease or increase in the measured adhesion according to the compound formed and the condition of ageing.

§ 1. INTRODUCTION

ONE of the main applications of thin films evaporated under high vacuum conditions is the formation of reflecting surfaces. Aluminium has been extensively used for this purpose because of its high efficiency as an optical reflector and its comparative resistance to atmospheric corrosion. It rapidly becomes covered by a thin transparent oxide film which does little to impair the optical reflectivity but, once formed, protects the film from further corrosion (Holland 1956). But aluminium deposited directly on to glass forms a film which is relatively weak mechanically. It is therefore common practice to underlay the aluminium with a thin layer of chromium which increases the durability and adhesion. The effect of the chromium underlayer has recently been investigated (Weaver and Hill 1958) and it has been considered of interest to investigate nickel and cobalt in the same way since there is more information on the intermetallic compounds formed between these metals and aluminium, and complete phase diagrams are available (Hansen 1936, Metals Handbook 1948) which should assist considerably in the interpretation of ageing effects.

§ 2. EXPERIMENTAL

The evaporation equipment used for preparation of specimens consisted of a 12 in. diameter glass bell jar evacuated by an oil diffusion pump which was backed by a rotary pump, giving pressures of $2-5 \times 10^{-5}$ mm Hg as measured by an ion gauge, in the vacuum chamber. The films were deposited on glass microscope slides which were cleaned by vigorous scrubbing with Teepol solution and rinsing under running water before

† Communicated by the Authors.

drying on a well-washed linen cloth. The slides were finally polished with lens tissue before placing them in a rotating jig in the vacuum chamber. Separate heaters, screened from each other, were used for the aluminium and for the nickel or cobalt, and the jig allowed the slides to be brought into position above each heater in turn, so that the metal could be evaporated on to the slide vertically above the heater at a distance of about 8 in. During the pumping cycle the full length of slide was exposed to a cleaning discharge for about 15 min. The slide was then rotated by the jig into a position above the heater used for the nickel or cobalt underlayer and when the pressure dropped to about $2-5 \times 10^{-5}$ mm Hg, a suitable thickness of film was deposited. A mask in front of the slide allowed one end only to be coated over the full width and for two-thirds of the length. The specimen slide was then rotated into position above the aluminium heater and an opaque film (approx. 600–800 Å) was deposited at a rate of about 20 Å/sec so as to cover the other end of the slide for two-thirds of the length. This meant that the films overlapped on the central portion of the slide which was thus coated with a two-layer film.

The underlayer was monitored during deposition and its final thickness was obtained by measuring the optical transmission using a barrier layer photocell to measure the intensity of a transmitted beam of white light. A calibration was made for each of the metals used, by weighing specimen films on a chemical microbalance and using the bulk density to calculate the thickness, so that effective weight thicknesses were obtained from the measurements. Any adsorption during the weighing might cause our thickness values to be slightly on the high side but no signs of such adsorption were observed.

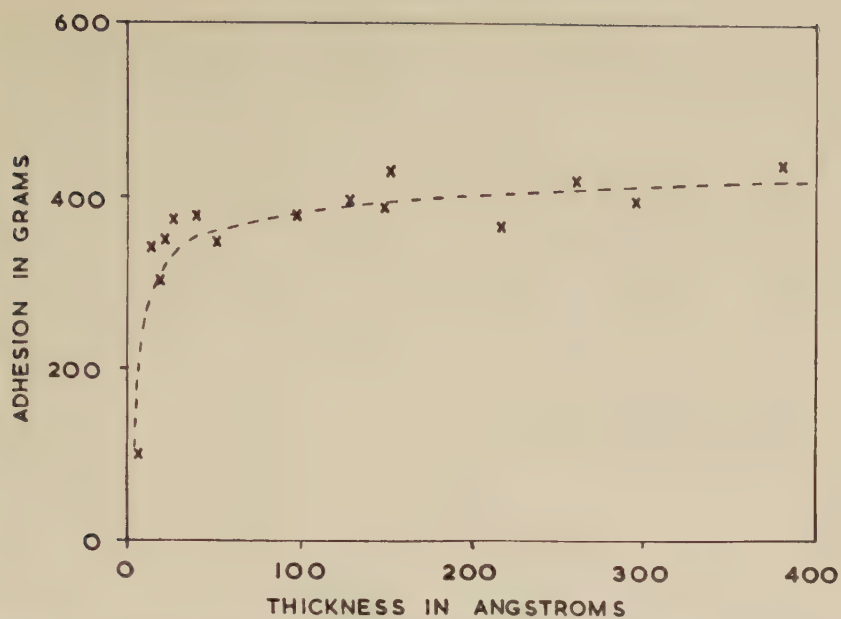
The specimen slides were removed from the vacuum chamber immediately after evaporation and measurements of adhesion were made on each of the three sections to obtain values for the aluminium, the double layer film, and the nickel or cobalt on its own. Some of the slides were then aged at room temperature and others were aged in hot-air ovens at 120°C, measurements of adhesion being repeated at suitable time intervals. The adhesion measurements were made by drawing across the film a loaded chrome steel point having a smoothly rounded tip as described by Heavens (1950) and analysed later by Weaver and Benjamin (1958). It was shown by Weaver and Hill (1958) in the case of chromium and aluminium that for double layer films the measurement is no longer dependent on adhesion alone. However, provided care is taken in the interpretation of results, information can be obtained from the ageing effects and the measurements will be referred to here as adhesion measurements even though this may not be strictly correct in all cases.

§ 3. RESULTS

3.1. *Nickel*

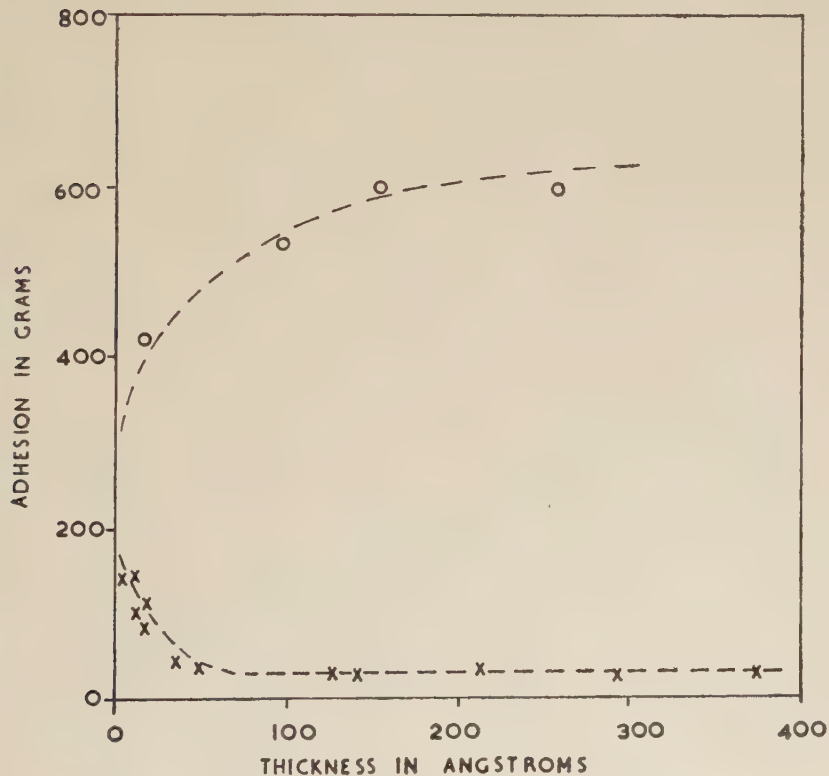
In previous work (Weaver and Hill 1958) on aluminium films with an underlayer of chromium, it was shown that the adhesion measured depended

Fig. 1



Variation of measured adhesion with thickness of nickel underlayer, immediately after evaporation.

Fig. 2



Variation of measured adhesion with thickness of nickel underlayer, after ageing.

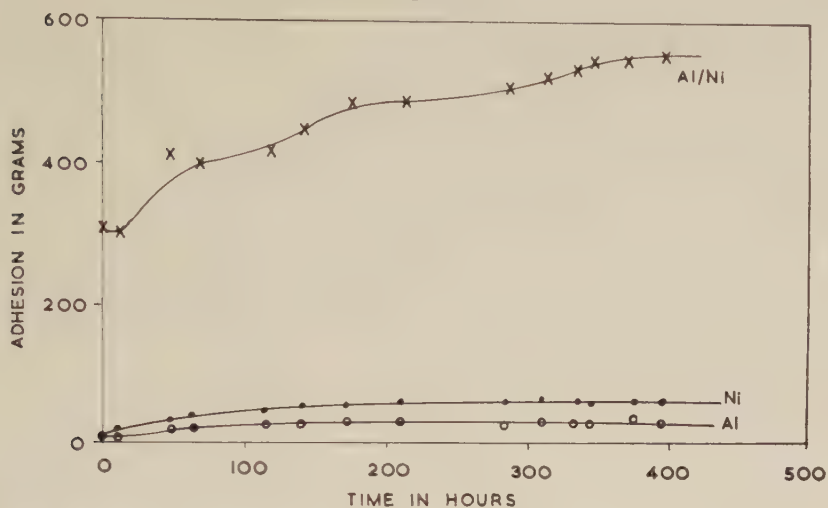
upon both the thickness of the underlayer and time. Figure 1 gives the results of measurements made immediately after evaporation on a number of specimens having different thicknesses of nickel under the aluminium top-layer. It can be seen that except for very thin films ($< 30 \text{ \AA}$) the figures obtained were fairly high and reasonably consistent. Some of the specimens were aged at room temperature for about two weeks and the results obtained after ageing are shown in the upper curve of fig. 2 where it can be seen that they follow the same general trend as the results for the unaged films shown in fig. 1, but the values are considerably higher. On the other hand, the specimens which were aged for three days at 120°C gave completely different results. The final measurements are shown in the lower part of fig. 2 and it can be seen that not only are all the results obtained considerably lower than for unaged films but also the highest values obtained are for the thinnest films. The thicker nickel films seem to have little effect upon the adhesion, as measured, and a double-layer film gives results which are little better than a pure aluminium film. This is not in accordance with our previous experience with chromium as an underlayer for aluminium, where ageing at 120°C appeared to produce the same final result as more prolonged ageing at room temperature.

Figure 3 gives ageing curves for aluminium, nickel and a double layer of aluminium on top of nickel, obtained for a typical specimen slide which was aged at room temperature. The pure aluminium and pure nickel films both show an increase in adhesion with time but neither has a good adhesion even after ageing. The two-layer film shows a rapid increase in the measured adhesion and the general shape of the curve closely resembles our previous results using chromium instead of nickel. The difference between the pure nickel and the two-layer film is even more pronounced and again it is impossible to explain the difference in terms of any change in the basic adhesion between the underlayer and the glass. The nickel below the aluminium is only a continuation of the pure nickel film and should have the same basic adhesion. Furthermore, the rapid initial increase occurs before aluminium could have diffused through the nickel to the glass surface. The shape of the ageing curve is once more typical of a diffusion precipitation process such as occurs in age-hardening (Gayler 1937, Smith 1949) and we are forced to conclude that the high measured adhesion of the double film is actually due to a layer of inter-metallic compound formed at the interface.

Curves were obtained in the same way for specimens aged at 120°C , and a typical set is shown in fig. 4. The single metal films of nickel and aluminium behave much as before, but the curve for the two-layer film rises rapidly to a peak and then falls away to a low value. It was also observed that the aged films were strongly aggregated. This suggests that the higher temperature of ageing causes an acceleration of the inter-metallic reaction which proceeds to completion and is followed by complete precipitation, resulting in an aggregated structure having very poor mechanical strength and an adhesion no better than a single nickel or single aluminium film.

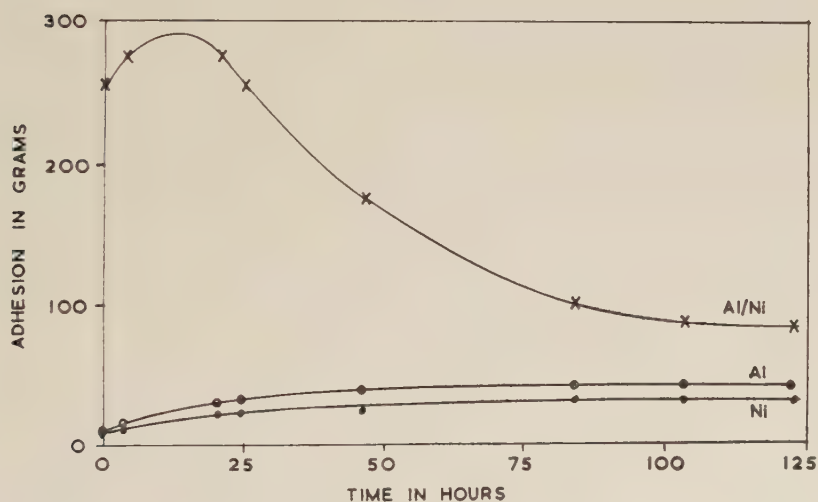
The existence of an intermetallic compound in films of the type used was confirmed by electron diffraction. Formvar films were prepared by dry stripping from a cleaned microscope slide of the type used and thin

Fig. 3



Ageing at room temperature for aluminium film with nickel underlayer.

Fig. 4



Ageing at 120°C for aluminium film with nickel underlayer.

films of nickel and aluminium were evaporated on to the formvar. The diffraction patterns for the single metals are shown in figs. 5 (a), 5 (b) (Pl. 42). The specimens were examined with the electron beam both normal and at 45° to the plane of the specimen but no signs of preferred

orientation were found. A further specimen was prepared by evaporating alternate thin layers of nickel and aluminium, the individual layers being about 10–20 Å thick. The diffraction pattern for this was obtained within 40 minutes of deposition and is shown in fig. 5 (c) (Pl. 42), where it can be seen that a new structure is present. The structure was found to correspond to the compound δAlNi .

It is considered most unlikely that the films could be affected by the electron beam during examination. In an electron diffraction investigation, more rapid hardening was found for aluminium–silver in the form of thin layers than was found for bulk material using x-ray diffraction. A temperature rise during examination was suspected but theoretical calculations (Winkelmann 1955) indicated that the maximum temperatures of the metal films would not exceed 31°C and the temperature of the supporting grid would not rise above 27°C. Later experimental measurements (Winkelmann 1956) on gold/copper foils gave temperature rises in agreement with theory, of about 10°C for beam currents between 5×10^{-6} and 2.5×10^{-4} amp/cm².

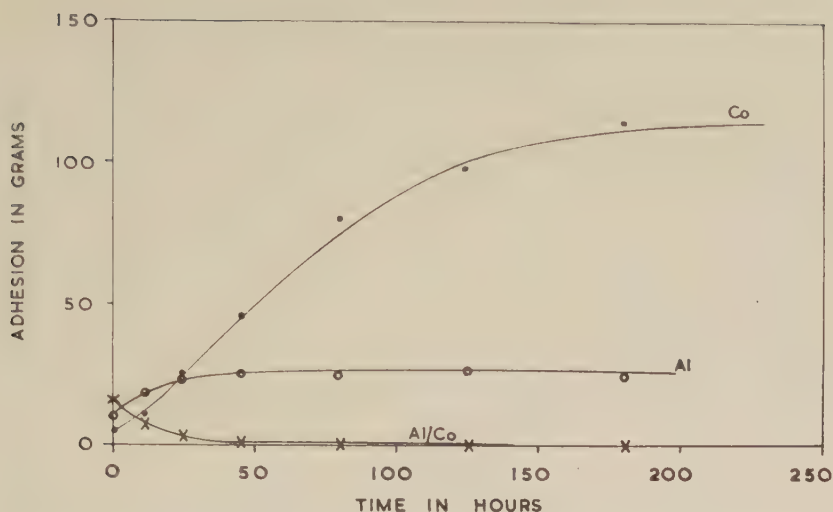
Temperatures of this order during the period of examination would not have any appreciable effect upon our results and the AlNi compound must have been formed before the film was exposed to the electron beam.

3.2. Cobalt

Specimen slides were prepared in the same way as for chromium and nickel and fig. 6 gives ageing curves which were obtained for a typical specimen which was aged at room temperature. The cobalt film alone had a higher adhesion than nickel but when overlaid by aluminium, no trace of this higher adhesion remained and the measured values dropped fairly rapidly to zero level. Corresponding results for a specimen aged at 120°C are shown in fig. 7, where it can be seen that the cobalt alone had an even higher adhesion than a film aged at room temperature but the addition of an aluminium overlayer again resulted in a film with poor adhesion, the rate of fall being accelerated. The variation of adhesion with the thickness of the cobalt underlayer is given in fig. 8 and in all cases the final adhesion is negligible.

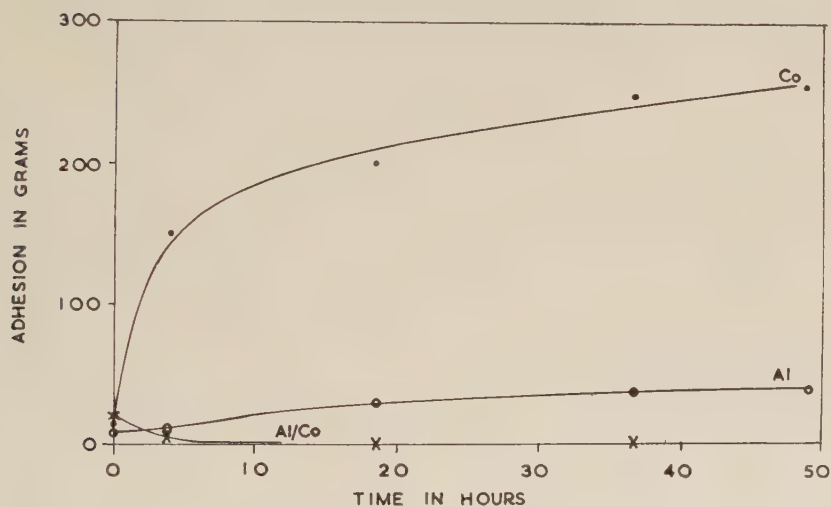
The ageing curves for pure cobalt films closely resembles the corresponding curves for pure chromium but as an underlayer for aluminium it is obviously ineffective. The phase diagrams for aluminium–nickel and aluminium–cobalt are very similar and in each case there is a pronounced peak corresponding to formation of a stable high melting point compound containing the two atoms in equal proportions. It would appear that the reaction which causes ageing of nickel–aluminium films at high temperatures to be ineffective proceeds even more readily in the case of cobalt and aluminium, resulting in complete precipitation and consequent aggregation even at room temperature. The aggregation in aged films may readily be seen.

Fig. 6



Ageing at room temperature for aluminium film with cobalt underlayer.

Fig. 7

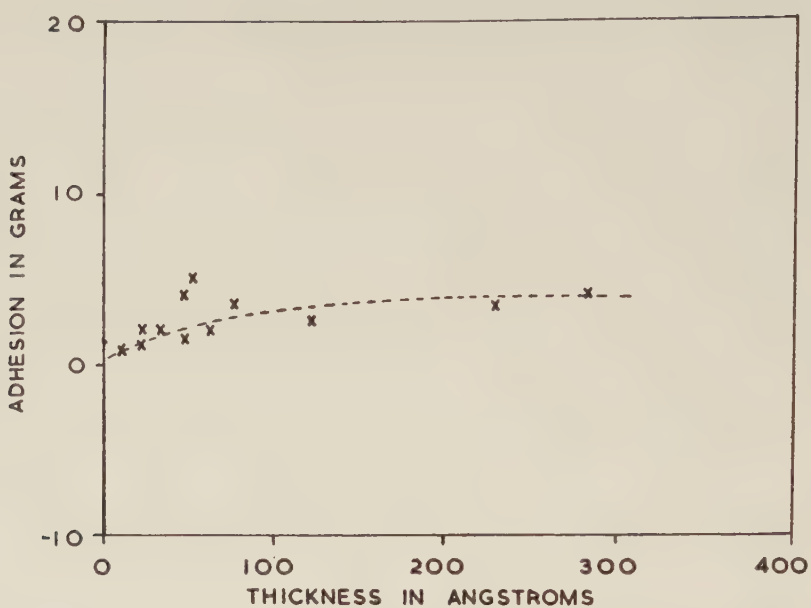


Ageing at 120°C for aluminium film with cobalt underlayer.

3.3. Chromel

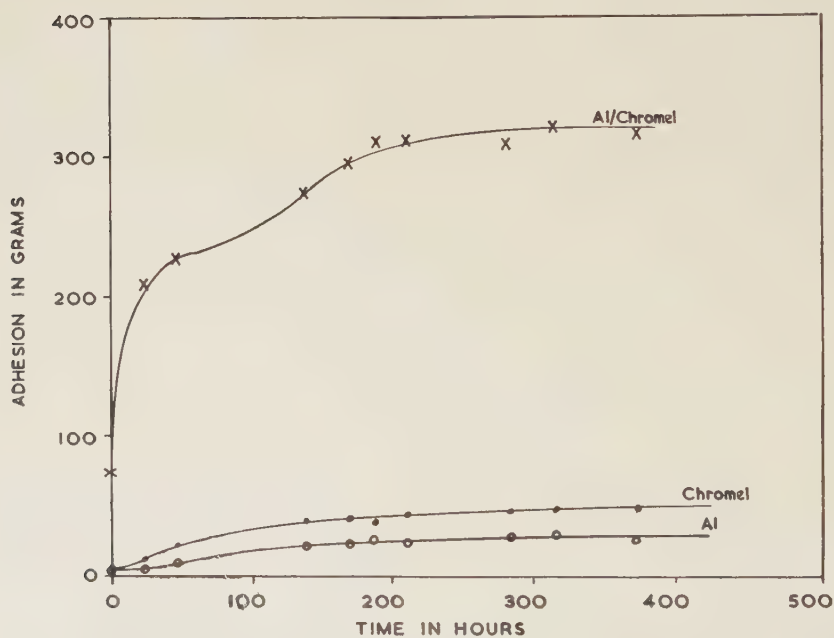
The results obtained with nickel and chromium led us to try chromel (80/20 Ni/Cr) as a possible underlayer for aluminium films, and fig. 9 shows curves which were obtained when ageing a specimen at room temperature. The graph for the two-layer film again shows the double step which has already been observed with chromium and nickel under similar conditions. A typical specimen aged at 120°C gave the results

Fig. 8



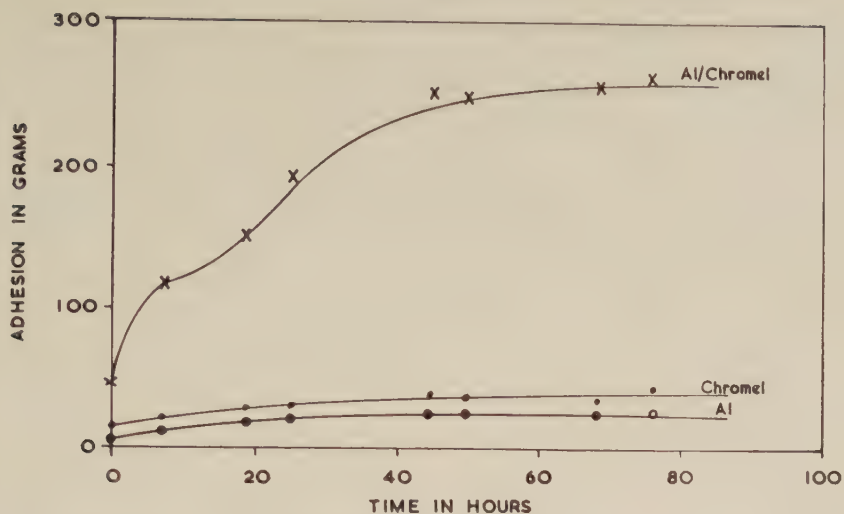
Variation of measured adhesion with thickness of cobalt underlayer.

Fig. 9



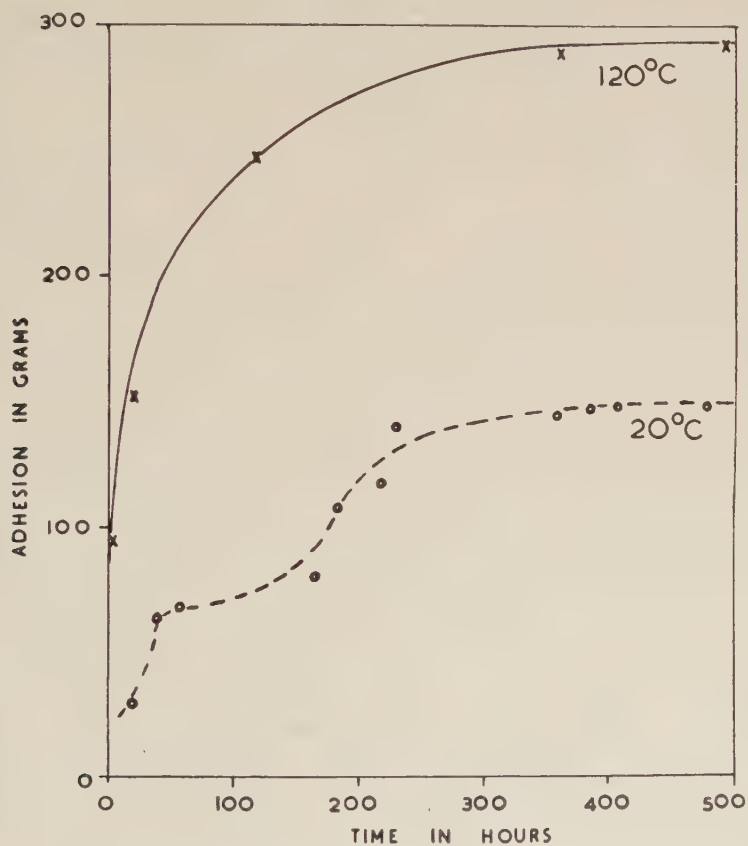
Ageing at room temperature for aluminium film with chromel underlayer.

Fig. 10



Ageing at 120°C for aluminium film with chromel underlayer.

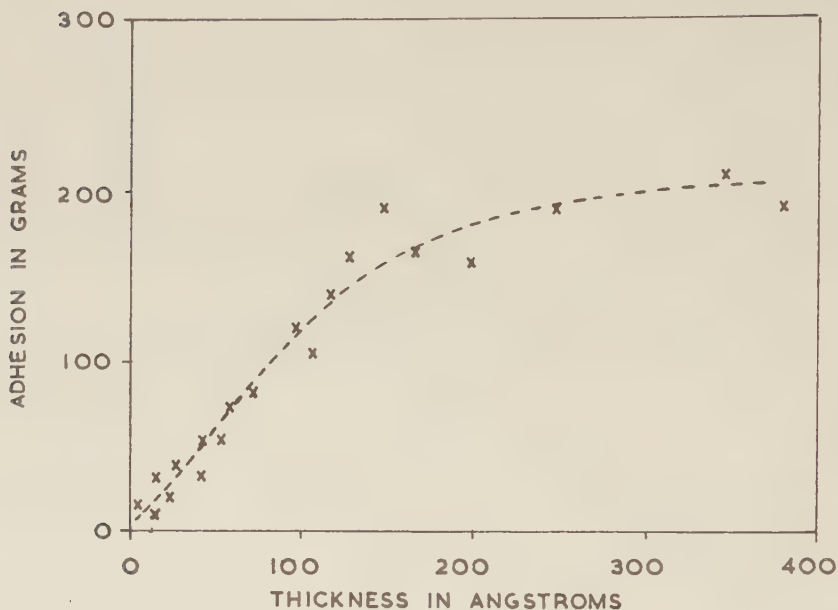
Fig. 11



Ageing of aluminium films with chromium underlayers.

graphed in fig. 10. The adhesion of the two-layer film again rose with time showing a double rise of the type which had previously been observed only in room temperature ageing. Curves which had been obtained earlier using pure chromium as an underlayer are given for comparison in fig. 11 and it can be seen that the final values reached are higher when chromel is used although not so high as can be obtained by using a nickel underlayer and ageing at room temperature. On the other hand, the poor performance of nickel at higher temperatures appears to be eliminated.

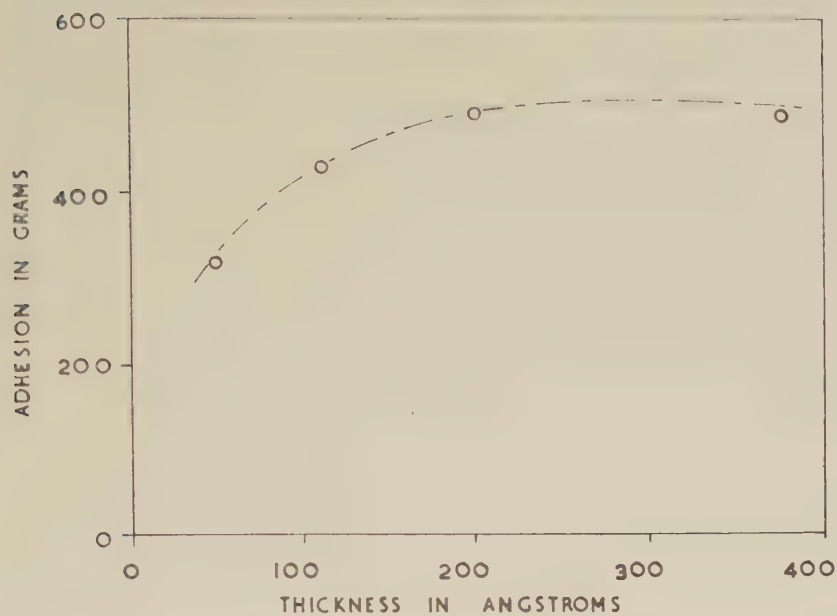
Fig. 12



Variation of measured adhesion with thickness of chromel underlayer, immediately after evaporation.

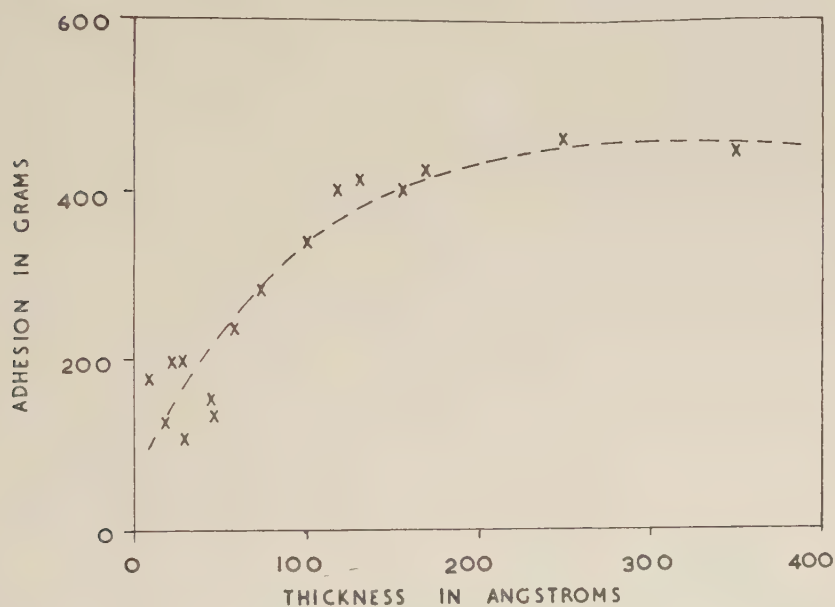
Figure 12 gives the results of adhesion measurements made on a large number of specimens immediately after evaporation to show the variation with thickness of the chromel underlayer. These results resemble those obtained with chromium rather than nickel but without the pronounced difference in effect between thin films and thick films which had previously caused a noticeable step increase in the graph at an underlayer thickness around 200–300 Å. This presumably is due to the nickel content of the alloy having a greater effect in the case of thinner films. The effects of ageing at room temperature and at 120°C are shown in figs. 13 and 14 respectively, where final results are plotted against thickness of underlayer. The temperature of ageing does not appear to be of great importance and the nickel content of the alloy allows thinner films to be used than would

Fig. 13



Variation of measured adhesion with thickness of chromel underlayer, after ageing at room temperature.

Fig. 14



Variation of measured adhesion with thickness of chromel underlayer after ageing at 120°C.

be effective with chromium and yet there is no decrease of measured adhesion when ageing at high temperatures.

§ 4. DISCUSSION

The curves showing ageing at room temperature for aluminium films with an underlayer of nickel closely resemble the results obtained previously using chromium as the underlayer. The differences between the measurements made on the three sections of one slide lead us to conclude again that our measurements on the double film are affected by an action at the interface between the nickel and the aluminium. The phase diagram for aluminium/nickel (*Metals Handbook* 1948) has a pronounced peak indicating formation of a stable compound AlNi containing the two metals in equal atomic proportions and this compound has been identified by electron diffraction in a multi-layer film formed by evaporating alternate thin layers of aluminium and nickel. A multiple film was used so that ageing would be rapid and the diffraction pattern of the compound would not be obscured by the rings of aluminium and nickel. The film was kept at room temperature and our results were obtained only 40 min after preparation indicating that the reaction must have started immediately after or during deposition. This AlNi compound will be formed in the same way at the interface between the aluminium and nickel of the specimens used for adhesion measurements. This is in accordance with our interpretation of the ageing curve obtained at room temperature with the double step indicating an age-hardening process of diffusion-precipitation. The AlNi compound is known to be extremely hard and strong and an intermediate layer formed in this manner would certainly give an increased strength to the film as a whole. In our method of testing this would tend to spread the load on our rounded point over a larger area so that the shearing stresses required to remove the whole film would only be obtained at much higher loads.

The phase diagrams (*Metals Handbook* 1948) for aluminium-cobalt and aluminium-nickel are almost identical and the ageing of an aluminium film underlaid by cobalt follows the general pattern observed with nickel when ageing at higher temperatures. In the case of cobalt the intermetallic reaction with aluminium would appear to proceed more readily and this is in agreement with the general chemical properties of the two metals. The results suggest that where a stable intermetallic compound of definite composition is formed, the reaction at the interface between two metallic films is likely to cause complete formation and precipitation of the compound with a resultant break-up of the original structure of the films, leading to pronounced aggregation and lack of adhesion to the substrate. This is most marked in the case of cobalt but occurs also with nickel at higher temperatures.

On the other hand, these effects have not been observed with chromium at either temperature of ageing and yet chromium is not markedly less reactive. This leads us to doubt our earlier suggestion that this metal

forms a preferential compound with aluminium similar to those of nickel and cobalt. The phase diagram for aluminium-chromium given by Bradley and Lu (1937) does not appear to have been accepted by the American Society of Metals for inclusion in the *Metals Handbook* but their classification of the α phase as a solid solution having a limiting composition would explain the differences in our results between chromium and the other two metals. The existence of a structure differing from either chromium or aluminium was shown by electron diffraction. If this corresponded to the limiting stage of a solid solution in which chromium atoms were replaced by aluminium with a steady increase in lattice spacing, then this structure could be obtained by gradual diffusion without excessive disturbance of the lattice but with an increasing strain causing progressive hardening. A process of this nature would be unlikely to result in the extensive precipitation and aggregation observed for cobalt and to some extent for nickel, where the reactions would be more vigorous. The age-hardening can, however, be more effective where a definite compound is formed provided the precipitated particles do not reach the critical size beyond which coherency strains are released as precipitation occurs. This can be seen in the case of nickel when ageing double films at room temperature. The increase in adhesion was much greater than a chromium underlayer had produced under similar conditions but the ageing curves obtained with nickel at higher temperature showed that the process was liable to get out of control.

The results obtained using chromel are interesting since it gave increases in adhesion which were comparable with the best results obtained with nickel, and noticeably greater than could be obtained with chromium. This was obviously due to the nickel content of the alloy leading to formation of the hard AlNi compound. Increasing the temperature of ageing had little effect upon the results obtained and this would seem to be due to the chromium content of the alloy. Interdiffusion of aluminium and this alloy would lead to simultaneous formation of the AlNi compound and the α phase of aluminium/chromium in an intimately mingled matrix from which only small particles of AlNi would be able to precipitate. Their growth would be severely limited so that the release of coherency strains which had been observed during the high-temperature ageing of nickel specimens would be unable to take place. Consequently, the age-hardening associated with nickel could be obtained without any progressive deterioration of properties even when ageing at higher temperatures.

From the practical point of view chromel has considerable advantages over nickel or chromium since it is relatively easy to evaporate and only a thin film of the alloy is required. The exact composition of the evaporated films may differ somewhat from the original alloy and is likely to vary slightly with the temperature of the heater but conditions do not appear to be critical. Careful control of the ageing temperature is obviously not necessary and rapid ageing is possible without any disadvantages.

ACKNOWLEDGMENTS

In conclusion we wish to thank Mr. J. W. Sharpe for his assistance with the electron diffraction photographs and one of us (R. M. H.) wishes to acknowledge the assistance of the Caird Trust in providing a post-graduate research grant.

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CORRESPONDENCE

The Fatigue of Metals at 1.7°K

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[Received September 16, 1958]

A RECENT paper (McCammon and Rosenberg 1957) showed that, at temperatures down to 4.2°K , metals which did not exhibit a ductile-brittle transition behave under fatigue in a fashion very similar to that which is exhibited if the fatiguing is carried out at room temperature. The main difference in behaviour was that for failure to occur in a given number of cycles, the alternating stress had to be increased as the temperature of the test was reduced. Even between 20.4 and 4.2°K a considerable increase in stress was necessary. It was also shown that the increases in stress which were required at low temperatures corresponded very well with the increases in the ultimate tensile strength of the metal which were also observed at these temperatures.

It seemed of interest to continue this investigation at temperatures below 4.2°K to see whether a further increase in fatigue strength would occur and the present note reports the results of these investigations.

Temperatures below 4.2°K were obtained by pumping the liquid helium in which the specimens were immersed. The apparatus had to be modified in order to do this so that no constant compressive stress, due to atmospheric pressure, was applied to the specimen. This was achieved by incorporating the whole of the vibrating unit in the pumping system. Details of the modification are given by McCammon (1957) and Rosenberg (1958). With the pump available it was possible to do fatigue tests at about 1.7°K .

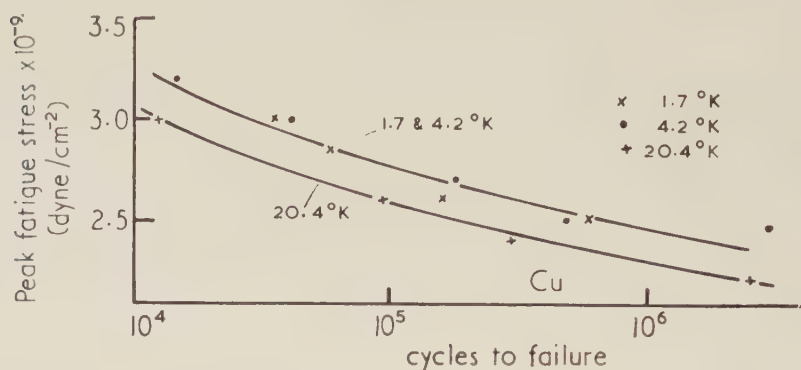
Tests were made on annealed O.F.H.C. copper and cadmium polycrystals and both showed that within the limits of experimental error there is no difference in the fatigue behaviour between 4.2 and 1.7°K . The results are shown in figs. 1 and 2 in the form of curves of S against $\log N$. Even in the case of cadmium, which of all the metals which we have investigated showed the greatest change in fatigue strength between 20.4 and 4.2°K , there is no significant change below 4.2°K . Tests with a carbon resistance thermometer attached to the specimen showed that there was no measurable temperature rise as the specimen was fatigued.

In view of the strong correspondence which has been observed between the fatigue and the ultimate tensile strengths it would seem reasonable to

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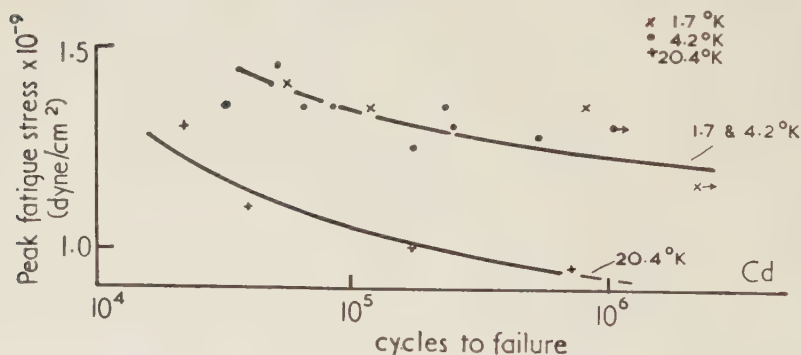
suppose that below 4.2°K there would be no detectable change in the tensile strength; i.e. somewhere in the range between 20.4 and 4.2°K the tensile strength (and the general work-hardening characteristics) flatten off to a constant value. Experiments at 4.2°K can thus be considered to give the limiting values for the various mechanical properties. Metals with very low melting points or characteristic temperatures may of course be exceptions.

Fig. 1



Curves of fatigue stress against the number of cycles to failure for copper, taken at 20.4 , 4.2 and 1.7°K .

Fig. 2



Curves of fatigue stress against the number of cycles to failure for cadmium, taken at 20.4 , 4.2 and 1.7°K .

This work was done during the tenure of British Oxygen Company fellowships by R. D. McCammon and R. K. MacCrone.

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The Magnetic Susceptibility of Ferrous Fluosilicate at Low Temperatures

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[Received September 24, 1958]

§ 1. INTRODUCTION

The crystal of ferrous fluosilicate has rhombohedral symmetry and there is one ferrous ion per unit cell. This ferrous ion is surrounded by a slightly distorted octahedron of water molecules. If the distortion is a squashing along a three-fold axis of the octahedron (the axis of the crystal) then the action of the cubic electrostatic field and the trigonal field due to the distortion together with the spin-orbit coupling will result in the $3d^6^5D$ state of the Fe^{++} ion being so split that the lowest level is non-degenerate with two two-fold levels at distances ϵ and 4ϵ above it. On the other hand, if the distortion is an elongation the lowest level is expected to be a two-fold level.

Paramagnetic resonance signals observed in ferrous fluosilicate at $20^\circ K$ have been reported by Baker and Bleaney (quoted by Bleaney and Stevens 1953) but have not been interpreted. The observation of a signal is consistent with the second alternative mentioned above and also with the first provided that the separation ϵ is small or at most comparable with $k \times 20^\circ$, so that the second level is occupied at the temperature of the observations. Measurements of the magnetic susceptibilities of the crystal parallel and perpendicular to the trigonal axis as a function of temperature can determine which of the two level schemes is the correct one as the expected variation of susceptibility with temperature is quite different in the two cases. Observations of $\chi_{||}$ and $\chi_{\perp}$ from $T = 77^\circ K$ to $T = 1.6^\circ K$ show quite clearly that the first case (squashed octahedron) is the one actually present in ferrous fluosilicate.

§ 2. METHOD

Measurements of the susceptibility of the salt parallel and perpendicular to the trigonal axis were made with a Sucksmith balance, with the specimen directly immersed in liquid helium or liquid hydrogen. In addition measurements were also made with helium gas in the inner Dewar vessel with the latter soft and with liquid nitrogen in the outer Dewar. The specimen was in the form of an approximate sphere with two small plane areas respectively parallel to the trigonal axis (natural face) and perpendicular to it (ground on a Tutton grinding goniometer). The specimen was optically adjusted in the field of an electromagnet to give $\chi_{\perp}$ and $\chi_{||}$. The salt was prepared from Specpure iron and was kindly supplied by Dr. J. M. Baker of the Clarendon Laboratory, Oxford.

† Present address : Royal Military College of Canada, Kingston, Ontario.

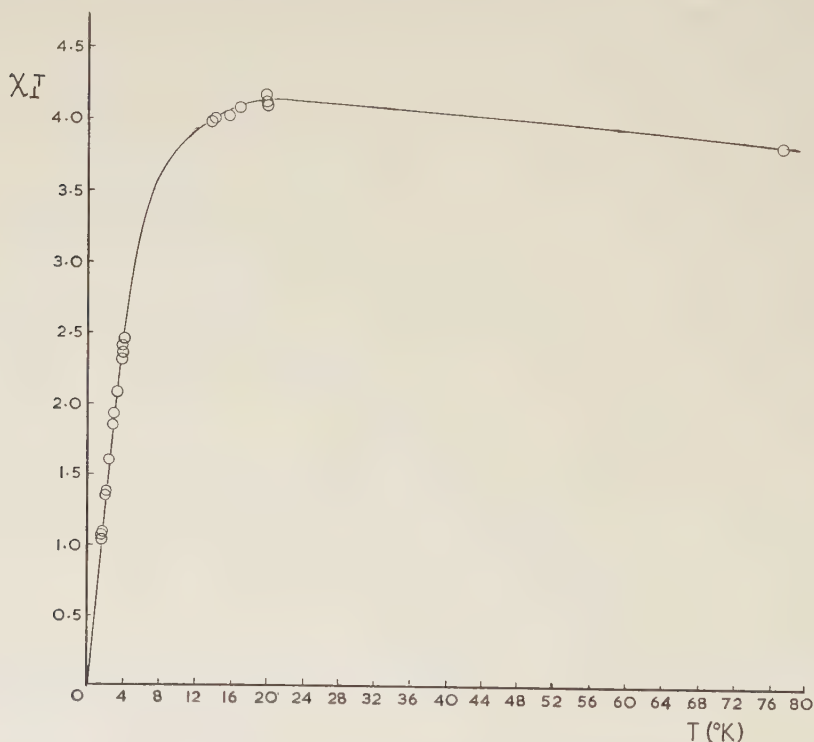
At the lower temperatures the values of $\chi_{\perp}$ were so much greater than those of $\chi_{\parallel}$ that it was necessary to correct $\chi_{\parallel}$ for cross susceptibility terms. Making acceptable assumptions regarding the symmetry of the non-homogeneous field of the electromagnet and assuming that the sphere is placed at the position of maximum force, this force is given by†

$$F = \frac{4\pi r^3}{3} H \cdot \frac{\partial H}{\partial z} \left[\chi_x - \frac{1}{5} (\chi_x + \chi_z) \left(\frac{r}{H} \frac{\partial H}{\partial z} \right)^2 \right]$$

where r is the radius of the sphere and if $\chi_{\parallel}$ has been oriented parallel to the axis of the magnet, then $\chi_x = \chi_{\parallel}$, $\chi_y = \chi_z = \chi_{\perp}$. At 77°K where $\chi_{\parallel}$ and $\chi_{\perp}$ are comparable, each has to be increased by about $\frac{1}{3}$ to $\frac{1}{2}$ % because of the correction. At 1.6°K the correction to $\chi_{\perp}$ is quite negligible but that to $\chi_{\parallel}$ rises to 40%. In view of this large correction and the small values of the susceptibility the data for $\chi_{\parallel}$ cannot be very precise at the lowest temperatures. The values of $\chi_{\perp}$ are accurate to about 1%.

§ 3. RESULTS

Four sets of observations on $\chi_{\parallel}$ and $\chi_{\perp}$ were made on three different crystals. The results for $\chi_{\perp}$ are shown in the figure where $\chi_{\perp}T$ is plotted



against T , the full curve being the theoretical expression (2) for the case $T_1 = 15.7^\circ\text{K}$; $\epsilon = 10.9 \text{ cm}^{-1}$; $\alpha = g_{\perp}^2/g_{\parallel}^2 = 1.13$; $g_{\perp} = 2.12$; $g_{\parallel} = 2.00$. It will

† M. H. L. Pryce, private communication.

be seen that there is a good agreement between the theoretical curve and the observed points. The table shows the observed values of $\chi_{\parallel}$ (column 2)

T ($^{\circ}\text{K}$)	$\chi_{\parallel}$ (expt)	T/T_1	$\chi_{\parallel}$ (calc)
77.3	0.0292	4.92	0.0301
20.4	0.0452	1.30	0.0469
14.2	0.0463	0.904	0.0474
7.85	0.0400	0.500	0.0412
4.2	0.0171	0.267	0.0178
3.14	0.0092	0.200	0.0064
1.57	0.0040	0.100	0.0005

together with the theoretical values (column 4) calculated with the above given values of the constants from expression (1)†. The agreement is certainly within the expected accuracy for $\chi_{\parallel}$. Part of the difference at the lowest temperatures may be due to the omitted constant term but Palumbo's calculations (see p. 272) suggest the latter is negligible in the present case.

The crystal is very anisotropic. The ratio of $\chi_{\perp}/\chi_{\parallel}$ rises from about 1.7 at 77°K to 4.5 at 20°K and 160 at 1.6°K. On the other hand, the average susceptibility $\frac{1}{3}(\chi_{\parallel} + 2\chi_{\perp})$ fits the Weiss law $\chi(T+1) = \text{const}$ down to at least 14°K, showing clearly the loss of available information when only the susceptibility of the powdered salt is measured.

§ 4. DISCUSSION

Under the action of a cubic crystal electric field the $3d^6 5D$ state of the Fe^{++} ion splits into two levels, approximately 10 000 cm^{-1} apart. The trigonal component of the field of the squashed octahedron of water molecules then splits the lower of these two levels into two further levels separated by a distance δ . The spin orbit coupling finally splits the lower of these two levels into a singlet lowest, followed by two doublet levels at ϵ and 4ϵ respectively above the singlet. As ϵ is expected to be of the order of 10 cm^{-1} and δ much larger, a first approximation to the low temperature susceptibility can be obtained by considering only these three lowest levels. The expressions for the susceptibility parallel and perpendicular to the trigonal axis of the crystal are as follows‡:

$$\chi_{\parallel} = \frac{2N\beta^2 g_{\parallel}^2}{kT} \left[\frac{\exp(-x) + 4\exp(-4x)}{1 + 2\exp(-x) + 2\exp(-4x)} \right] + \text{small const.} \quad (1)$$

$$\chi_{\perp} = \frac{2N\beta^2 g_{\perp}^2}{3kT_1} \left[\frac{9 - 7\exp(-x) - 2\exp(-4x)}{1 + 2\exp(-x) + 2\exp(-4x)} \right] + \text{small const.} \quad (2)$$

$$kT_1 = \epsilon, \quad x = T_1/T, \quad \alpha = \frac{g_{\perp}^2}{g_{\parallel}^2}. \quad \dots \dots \dots (3)$$

† In each case the small constant term has been omitted in calculating $\chi_{\perp}$ and $\chi_{\parallel}$.

‡ M. H. L. Pryce, private communication; see also M. H. L. Pryce, *Lezioni di Varenna*, in *Suppl. Nuovo Cim.*, **6**, 817 (1957).

Thus $\chi_1 T/\alpha$ is a predicted function of T/T_1 and the values of T_1 and α can be read directly from the ordinate and abscissa of the maximum of this curve, the values quoted on p. 270 being obtained in this way. As the $\chi_1 T-T$ curve fits the data very well and the $\chi_{II} T-T$ curve as well as can be expected, there is no doubt that the distortion of the octahedron in ferrous fluosilicate is a squashing. There is no agreement between the experimental data and the theoretical curves for the case of an elongation.

The theoretical problem has been examined in greater detail by Palumbo (1958) who has been able to derive ϵ as 10.9 cm^{-1} and δ as about 1200 cm^{-1} . The agreement between the experimental data and the more detailed theory remains excellent.

ACKNOWLEDGMENT

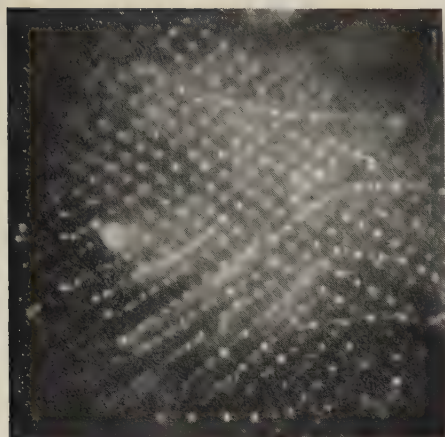
I am indebted to Professor M. H. L. Pryce for drawing my attention to the problem and for giving me access to his theoretical treatment before publication.

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- BLEANEY, B., and STEVENS, K. W. H., 1953, *Rep. Progr. Phys.*, **16**, 108.
PALUMBO, D., 1958, *Nuovo Cim.*, **8**, 271.

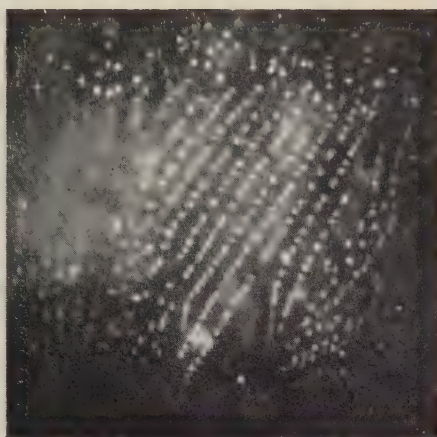
[The Editors do not hold themselves responsible for the views expressed by their correspondents.]

Fig. 1



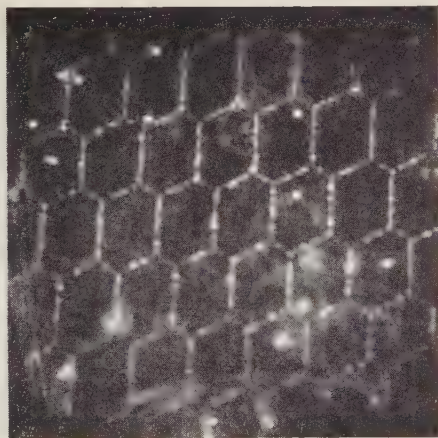
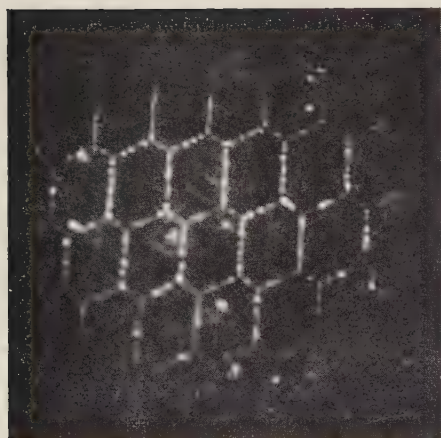
A rhombic net, formed by two arrays of dislocations, and decorated only at the nodes. $\times 1200$.

Fig. 2



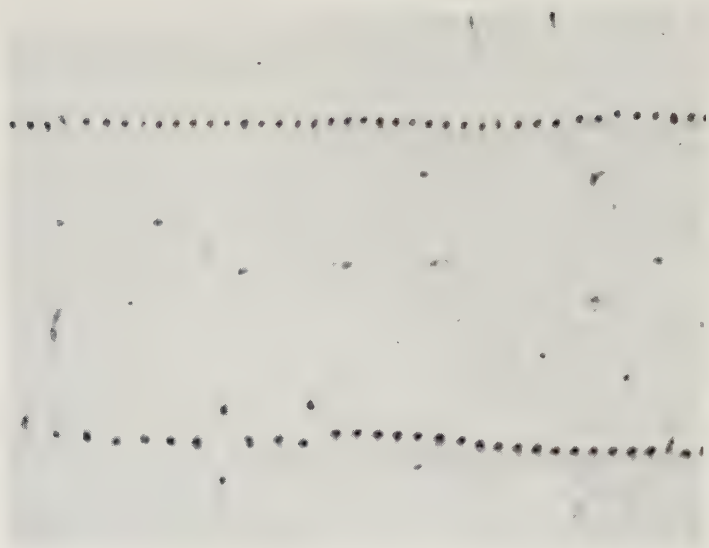
Dislocation lines of a tilt boundary decorated with discrete scattering particles. $\times 1200$.

Fig. 3



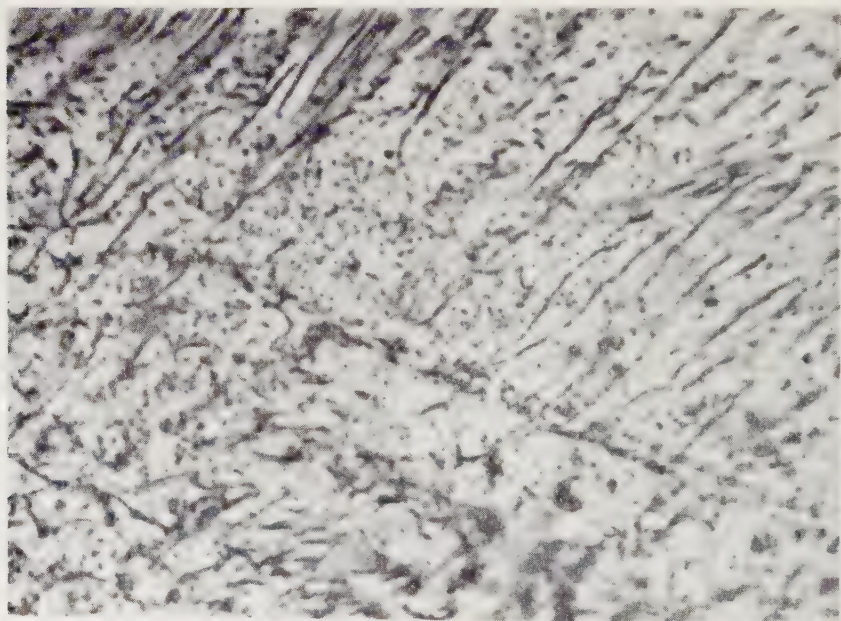
Hexagonal networks of dislocations photographed at a distance of 150 microns below the surface of the crystal. $\times 1200$.

Fig. 4



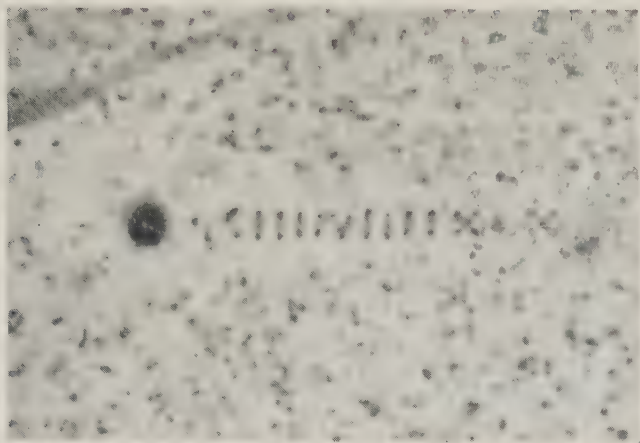
Tilt boundaries formed by edge dislocation lines normal to the surface in a specimen which had been recrystallized *in situ*. $\times 2400$.

Fig. 5



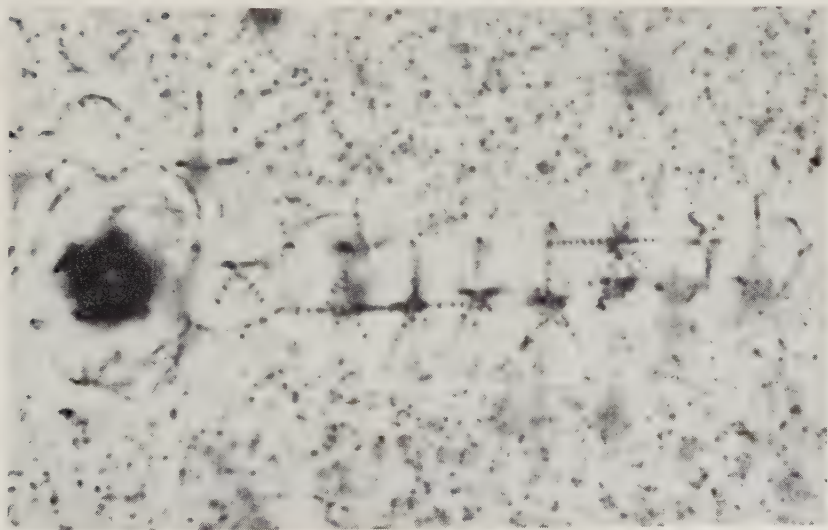
Arrays of dislocations associated with plastic deformation resulting from the application of a compressive stress. $\times 2400$.

Fig. 6



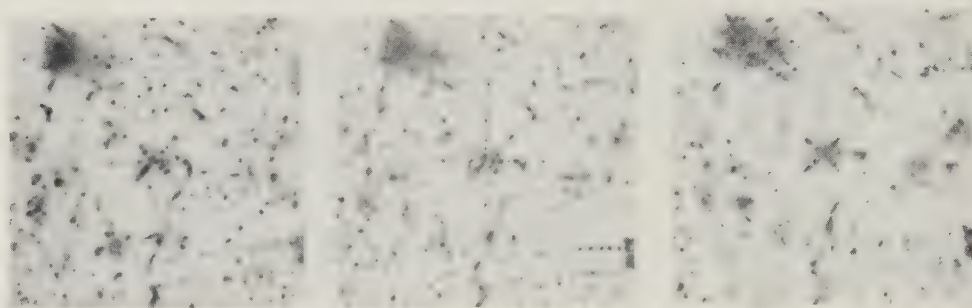
Prismatic and helical prismatic dislocations produced around a Hysil glass sphere of 2 microns diameter to relax the compressive stress arising during cooling. This should be compared with the left-hand branch of fig. 10. $\times 2400$.

Fig. 7



Prismatic dislocations produced by a Hysil glass sphere. Systems of similar dislocations on a much smaller scale, with axes along $\langle 110 \rangle$ directions, surround the larger decorating silver particles. $\times 2400$.

Fig. 8



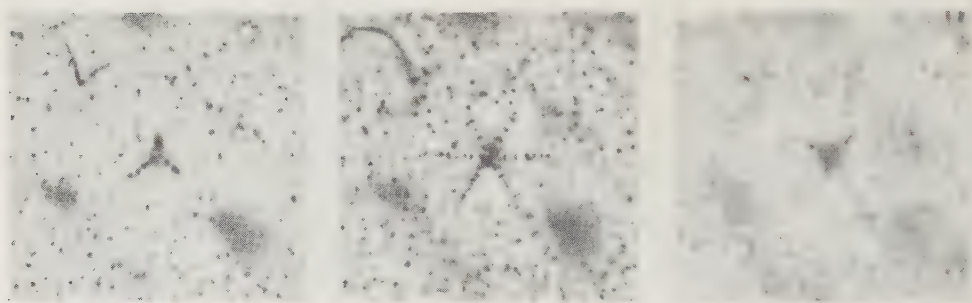
(a)

(b)

(c)

Prismatic dislocations extending along all twelve $\langle 110 \rangle$ directions around a particle of photolytic silver. A $[100]$ direction is normal to the plane of the photomicrograph and (a), (b) and (c) are separated along this direction by 5 micron intervals. $\times 1800$.

Fig. 9



(a)

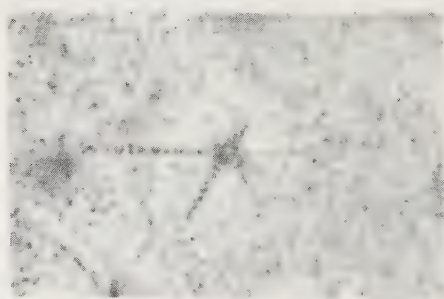
(b)

(c)

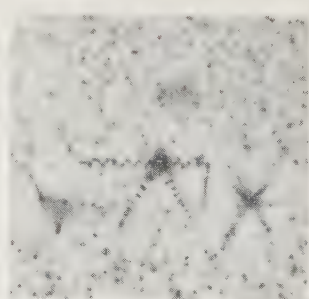
In this set, a $[111]$ direction is normal to the plane of the photomicrographs. Otherwise, the details are the same as for fig. 8. $\times 1800$.

Fig. 10

Fig. 11



The system extending to the left consists of a succession of prismatic dislocation loops and figures-of-eight. $\times 1800$.



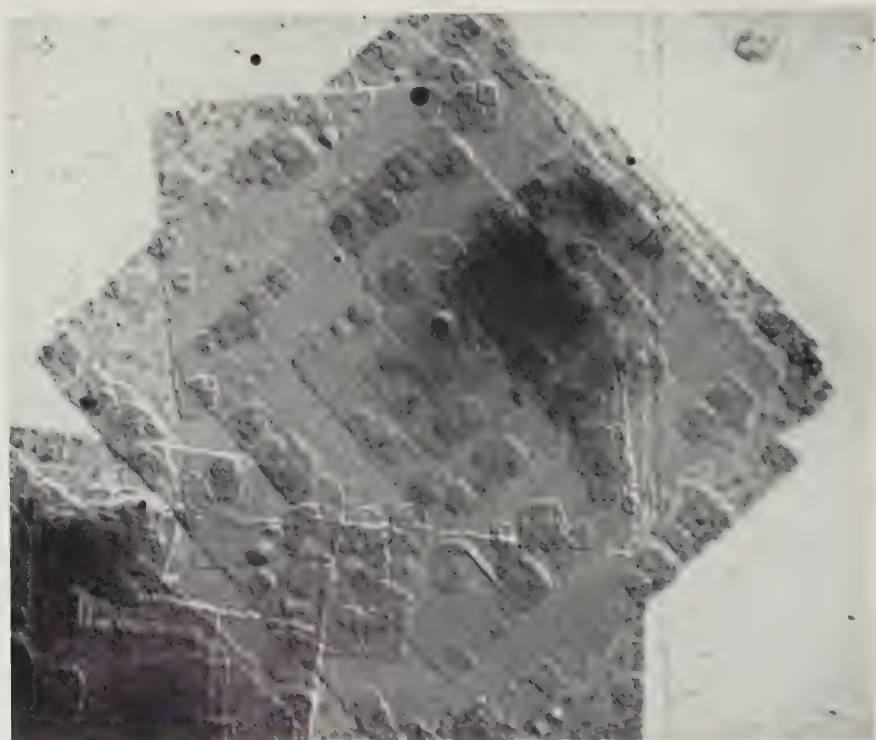
In this system, helical prismatic dislocations extend both to the right and to the left of the central particle. $\times 1800$.

Fig. 5



Electron micrograph of a square shaped crystal from xylene, Au-Pd shadowed.
 $\times 8000$.

Fig. 7



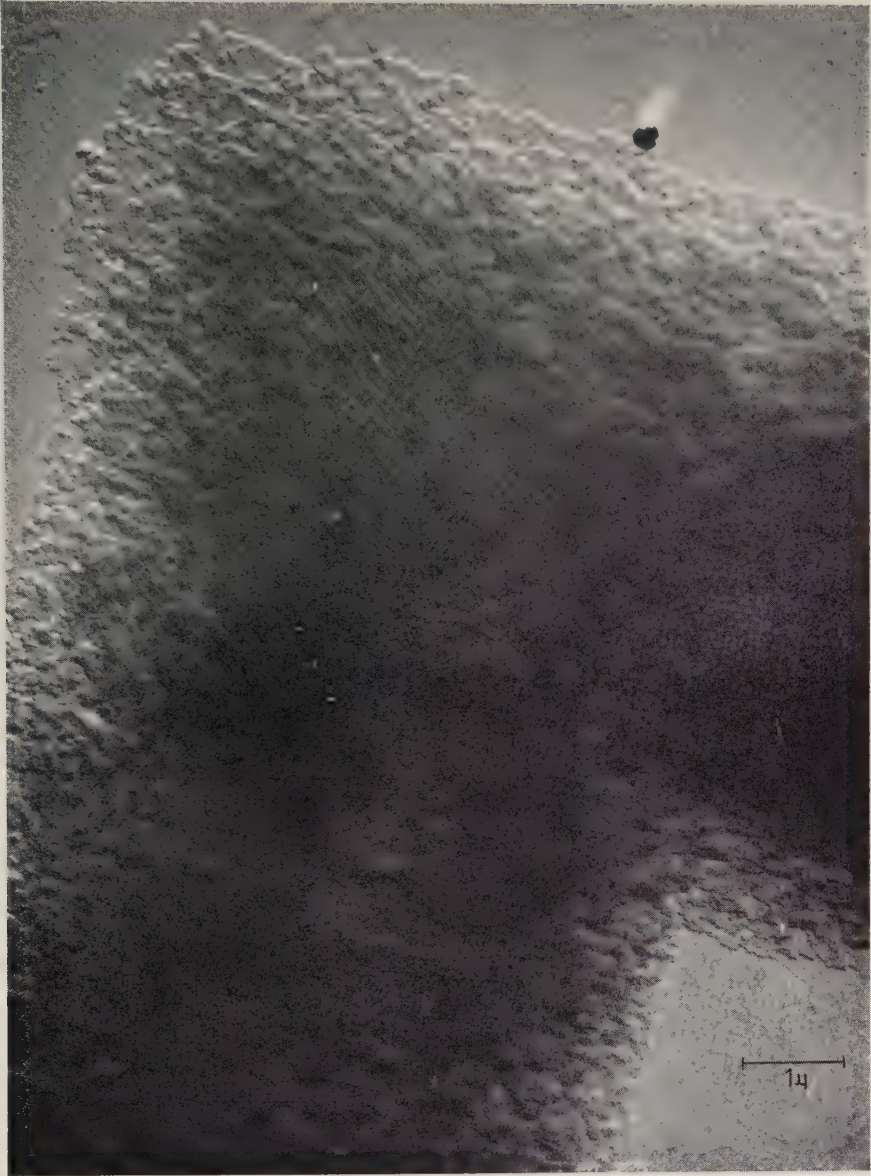
Electron micrograph of a square shaped crystal showing an accumulation of dislocations along the thinner terrace edges, Au-Pd shadowed. $\times 5900$.

Fig. 8



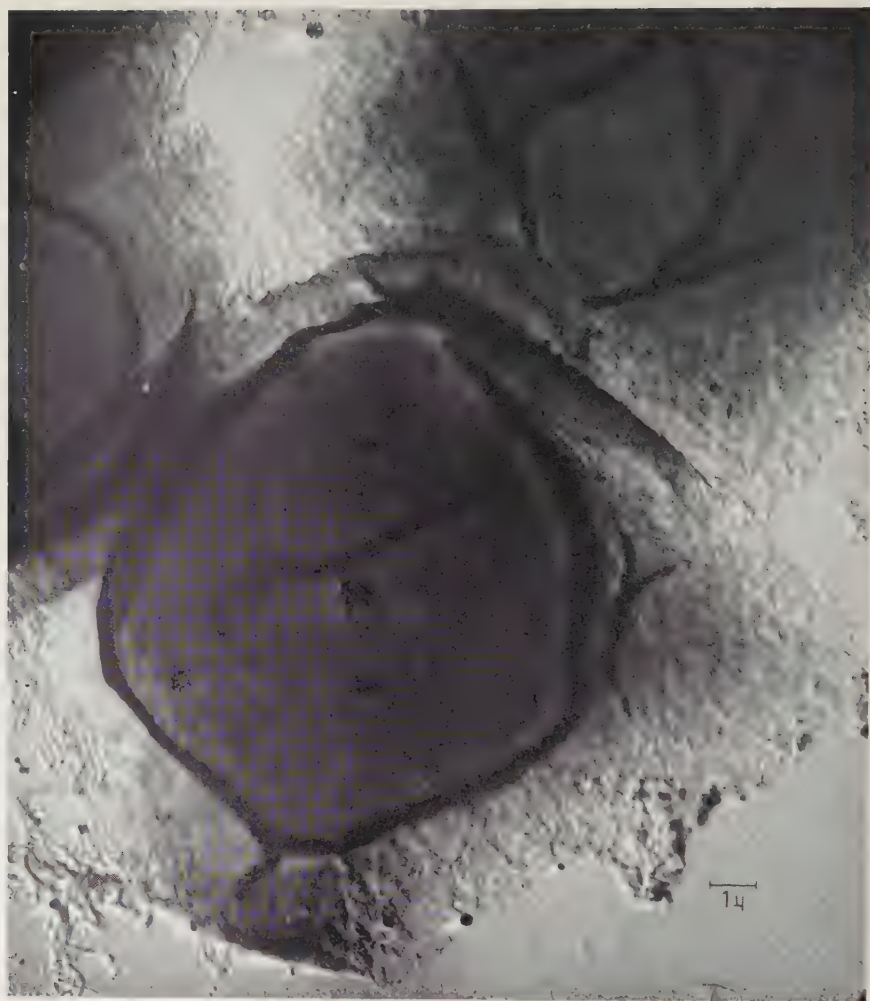
Electron micrograph of a square shaped crystal after having been heated to the melting point, Au-Pd shadowed. $\times 12\,500$.

Fig. 10



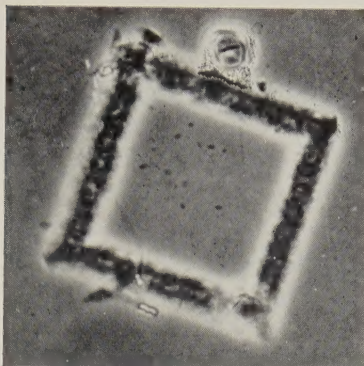
Detail of a picture-frame crystal. Electron micrograph, Au-Pd shadowed.
 $\times 13\,500$.

Fig. 11



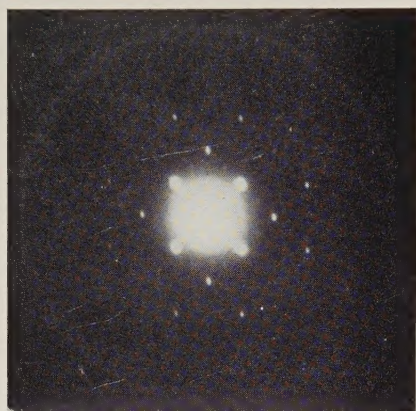
Malformed square crystals. Electron micrography, Au-Pd shadowed. $\times 6000$.

Fig. 9



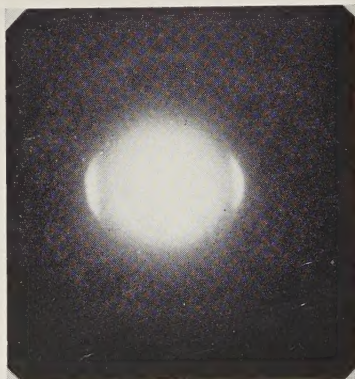
Picture-frame type crystal. Photo-micrograph. Phase contrast illumination. $\times 650$.

Fig. 12



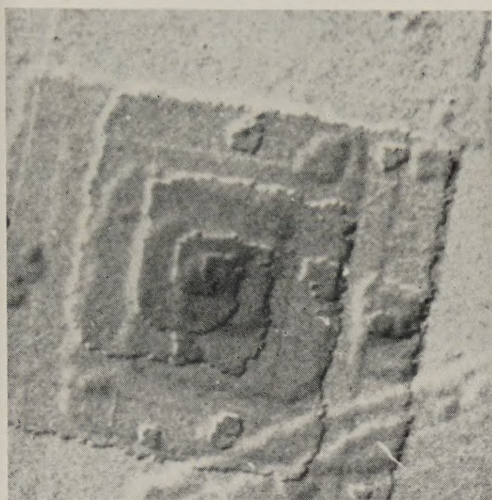
Electron diffraction pattern of a square shaped crystal. Beam perpendicular to the square layers. The corresponding square edges are at 45° to the vertical. The rings are due to the shadowing metal.

Fig. 16



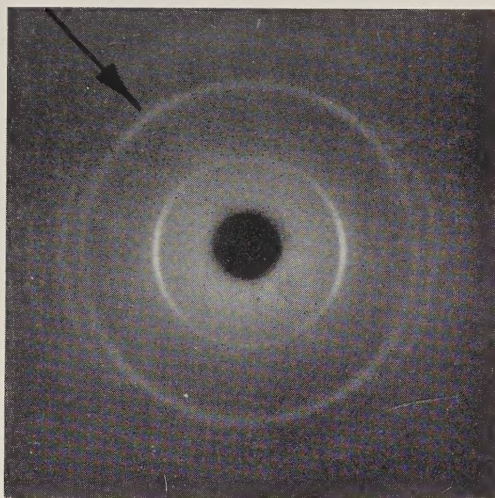
Electron diffraction pattern of a row of sheaves from trichlorethylene. Row direction vertical, fibril direction horizontal.

Fig. 6



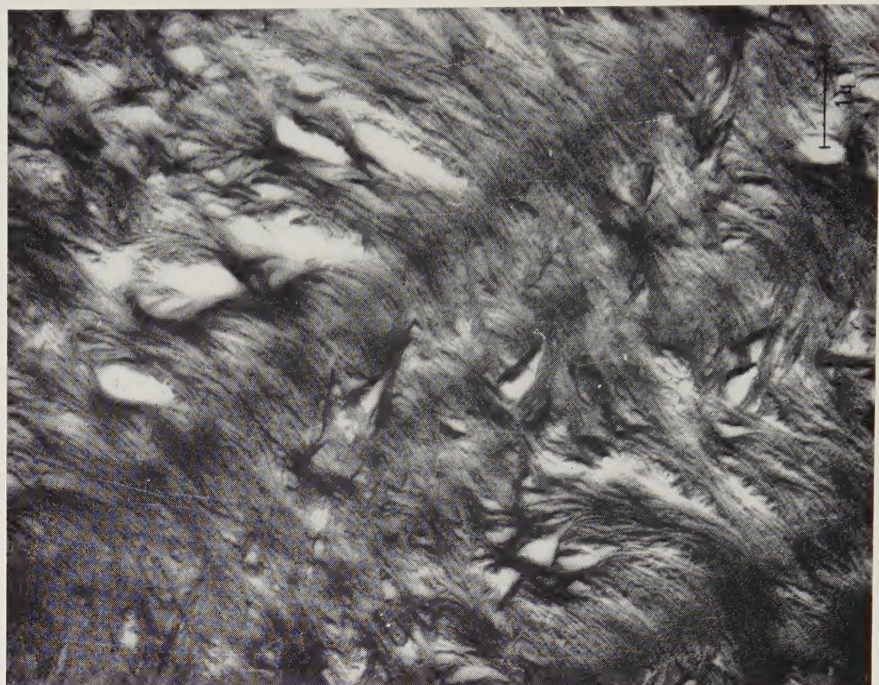
Centre of a double spiral in a square shaped crystal. Electron micrograph, Au-Pd shadowed. $\times 15\,000$.

Fig. 13



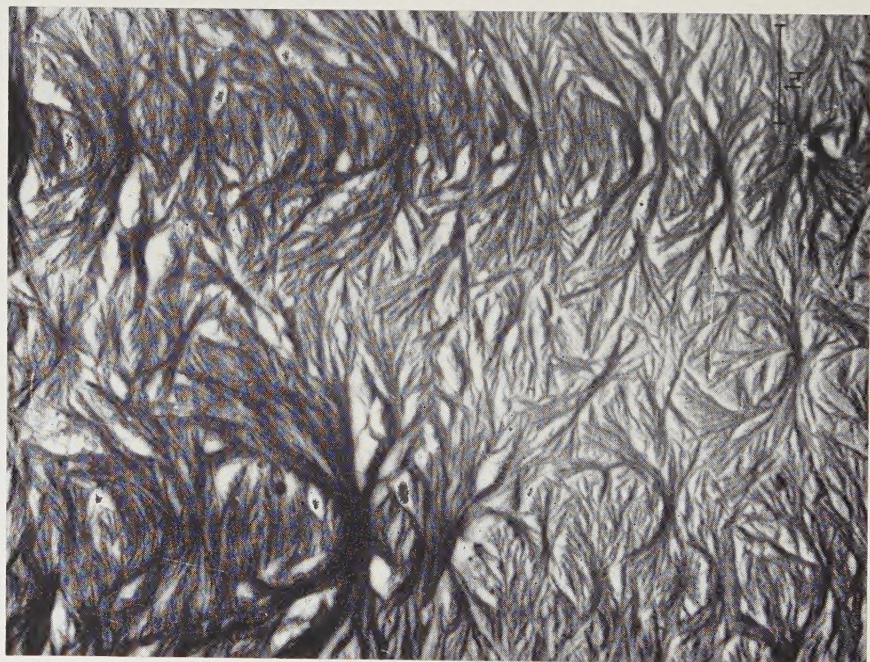
X-ray diffraction pattern of a film formed through the sedimentation of crystals as in fig. 11. Film-normal vertical.

Fig. 15



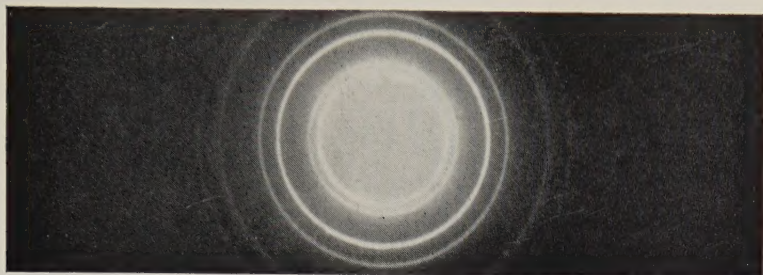
Similar preparation as in fig. 14, with a nearly parallel arrangement of fibrils. Electron micrograph, Au-Pd shadowed, $\times 13\ 000$.

Fig. 14

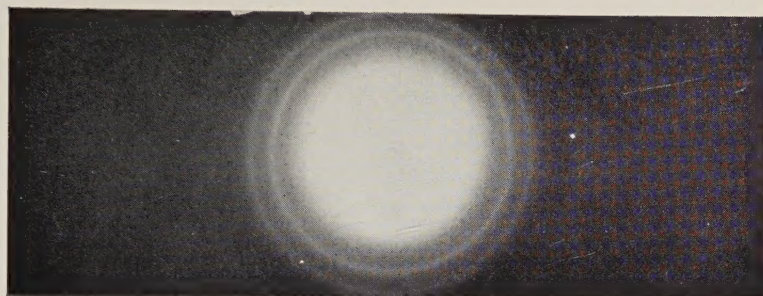


Electron micrograph of parallel sheaves formed from trichlorethylene, Au-Pp shadowed, $\times 13\ 000$.

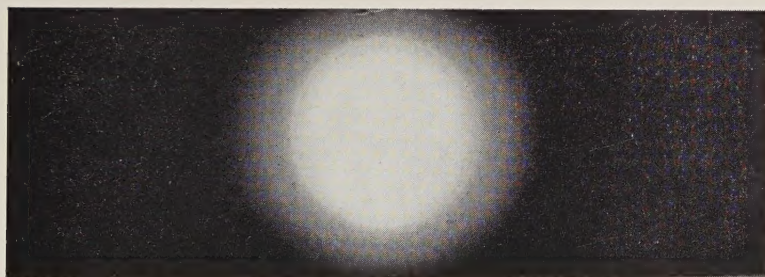
Fig. 5



(a)



(b)



(c)

Electron diffraction patterns. (a) Aluminium. (b) Nickel. (c) Nickel and aluminium giving δAlNi .

